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XXXVIII.—ON CERTAIN SUBSTANCES OBTAINED FROM TURMERIC.[1]

BY C. LORING JACKSON AND A. E. MENKE.

Owing to the difficulty of preparing curcumin, and the very unmanageable nature of the products obtained from it and from turmerol, we have not made as much progress in the study of these substances as we had hoped. In fact, we should not publish our results at the present time, were it not that we cannot continue the work together at all, and neither of us will be able to return to it for at least a year; we have therefore decided to collect in the following papers all the results we have obtained up to this time, although many of them are very fragmentary, and others consist only in indications which may prove useful in future work.

IV. CURCUMIN.

Action of Acetic Anhydride on Curcumin.

Monacetcurcumin, $C_{14}H_{13}(C_2H_3O)O_4$.—This substance is formed by the action of acetic anhydride and fused sodic acetate on curcumin, probably also by the action of acetylchloride. As has been stated in a previous paper,[2] it forms an uninviting brown

[1] Communicated by the Authors from the Proceedings of the American Academy of Arts and Sciences.

[2] This Journal, **4**, 90; and Proceed. Amer. Acad. **17**, 123.

resin, which we have not as yet succeeded in bringing into a crystalline condition; but nevertheless it can be obtained in a state of purity by the following method: Curcumin is heated on the water-bath with a slight excess of acetic anhydride and a little fused sodic acetate, for about sixteen hours, in a flask with a return-cooler; the dark brown viscous product is then dissolved in a little glacial acetic acid, and precipitated with water; after repeating the solution in acetic acid, and precipitation with water, the yellowish-brown precipitate is washed until free from acetic acid, and dried *in vacuo*.

0.1710 gram of substance gave 0.4178 gram of carbonic dioxide and 0.0922 gram of water.

	Calculated for $C_{16}H_{16}O_5$.	Found.
Carbon	66.67	66.62
Hydrogen	5.55	5.99

Properties.—A viscous brown mass without definite melting-point, although it shrinks together at 58°–60°, but it does not become fully liquid below 100°. It is soluble in alcohol and glacial acetic acid, essentially insoluble in ligroine and carbonic disulphide, slightly soluble in ether and in benzene; but its solubility in the latter is greater than that of curcumin. It dissolves in strong sulphuric acid with a blood-red color like that produced by curcumin. Aqueous sodic hydrate dissolves it, forming a red solution, which becomes decomposed, with the formation of ill-defined black products, when allowed to stand exposed to the air; a mixture of alcohol and sodic carbonate was reddened instantly by the substance, showing that the acetyl group had replaced the hydrogen of the phenol hydroxyl, as was to be expected; that is, its formula would be

$$C_6H_3(\overset{3}{O}CH_3)(\overset{4}{O}C_2H_3O)(\overset{1}{C}_6H_6COOH).$$

As has been stated already,[1] the substance gave unsatisfactory results when submitted to oxidation with potassic permanganate.

Diacetcurcumin, $C_{14}H_{12}(C_2H_3O)_2O_4$. — On one occasion the process described above yielded a yellow crystalline product instead of the brown viscous monacetcurcumin. The coming of the vacation interrupted our work before we had succeeded in determining the conditions on which the formation of this substance depends, the few experiments which we had time to try giving invariably monacetcurcumin; we must, therefore, for the present,

[1] *Loc. cit.*

confine ourselves to describing the properties and analysis of the substance. After the removal of the acetic anhydride and sodic acetate by treatment with water, it was purified by washing with alcohol and crystallisation from glacial acetic acid, dried at 100°, and analysed.

0.2230 gram of substance gave 0.5348 gram of carbonic dioxide and 0.1090 gram of water.

	Calculated for $C_{18}H_{18}O_6$.	Found.
Carbon	65.45	65.39
Hydrogen	5.45	5.43

Properties.—It crystallises from glacial acetic acid in rosettes of a vivid yellow color without the orange shade of curcumin, which are made up of very characteristic rhombic plates; melting-point 154°. It is more soluble in glacial acetic acid than in any other solvent, especially when the acid is hot; less soluble in alcohol than curcumin; slightly soluble in ether and benzene; essentially insoluble in ligroine and carbonic disulphide. Strong sulphuric acid dissolves it, becoming blood-red in transmitted light, green like rosaniline in reflected light; the red color is somewhat more purple than that produced by curcumin. Sodic hydrate in aqueous solution acts upon it very slowly, and not rapidly, even if dissolved in dilute alcohol; the red solution thus obtained gives with hydrochloric acid a viscous brown mass with a low melting-point, which seems to be impure monacetcurcumin. Sodic carbonic and alcohol give an orange solution looking like that of potassic dichromate. According to the formula given by us to curcumin in our first paper, this substance should be a mixed anhydride of curcumin and acetic acid, with the other acetyl group attached to the phenol oxygen, as in the monacet-compound,—a constitution which would be expressed by the following formula:

$$C_6H_3(OCH_3)(OC_2H_3O)(C_6H_4COOC_2H_3O).$$

That the carboxyl group is affected by the introduction of the second acetyl is shown by the fact that alkaline reagents act upon it only after some time, and then evidently decompose it; whereas the monacet-compound is attacked by them instantly, and the action consists only in the formation of a salt: but, on the other hand, the substance is more stable than acid anhydrides are usually, as is shown by this very action with alkalies, and by the fact that it can be boiled with water for many hours without

undergoing any change in melting-point, or the formation of any soluble acid.

Action of Phosphoric Oxychloride on Curcumin.

Of all the reactions of curcumin, which we have observed, this is by far the most striking, and we have decided therefore to describe it at some length, although we have not succeeded in determining the nature of the substance formed. If a few drops of phosphoric oxychloride are added to some curcumin suspended in ligroine, its orange-yellow color is converted instantly into a rich reddish purple, which in reflected light appears bronze-green with a metallic lustre, between the colors of rosaniline and Hofmann's violet. To prepare the substance in quantity, the curcumin was rubbed in a mortar with phosphoric oxychloride diluted with ligroine and afterward washed repeatedly with ligroine; the dark purple viscous mass thus obtained was dried in a desiccator over sulphuric acid, lime, and paraffine. This treatment, the best which we could devise, was usually far from effectual, as in every case but one the substance contained phosphorus, and was invariably converted during drying into a black mass having very different properties from the purple viscous substance at first obtained. The analysis of the substance free from phosphorus gave results less than one per cent. higher than those required by curcumin, and this was confirmed by the analysis of one of the preparations containing phosphorus, after the phosphorus present had been calculated as phosphoric acid, and subtracted from the weight of the substance.

The properties of the purple product are quite as striking as its formation from curcumin; for the addition of water converts it again into curcumin, and the change from purple to orange-yellow is instantaneous. That curcumin was formed in this case was shown by the melting-point, 178°. Alcohol also changes the color instantly from purple to yellow; but the product is much more soluble in alcohol than curcumin, and is possibly its ethyl ether. Ether acts in the same way, leaving, on evaporation, a viscous red mass; in ligroine and benzene it is essentially insoluble. By standing even in a desiccator it is gradually decomposed—more rapidly at 100°—into a black mass, which is unaffected by water, but soluble in alcohol or sodic hydrate, forming dark solutions. Owing to the uninviting properties of this decomposition product it was not studied further.

It is highly probable that the blood-red color imparted to strong sulphuric acid by curcumin is due to this substance, as curcumin is deposited when this solution is diluted. As to the nature of the purple substance, our analyses show nothing; but its easy conversion into curcumin by the addition of water indicates that it is an anhydride, and we are inclined to believe that the carboxyl of the curcumin alone is involved in the reaction, because we obtained a similar but somewhat redder color when monacetcurcumin was treated with phosphoric oxychloride.

In our first paper on curcumin we assigned to it the formula

$$C_6H_3(OH)(OCH_3)(C_6H_4COOH).$$

Our work since then has been directed toward the determination of the structure of the side-chain C_6H_4COOH, and, although we have not succeeded in proving anything about it definitely, we may be allowed to state that our results can be explained by the assumptions that the carboxyl is attached to the carbon atom next but one to the benzene ring, and that in the remainder of the side-chain some of the carbon atoms are united to form a ring.

TURMEROL.

In our first paper on this subject we mentioned that, although turmerol is converted into terephthalic acid by treatment with an excess of a hot solution of potassic permanganate, the same reagent produces, when cold and not in excess, one or more apparently new acids. In the following paper we describe our study of the product of this reaction, a complex mixture of acids, from which we have succeeded in isolating two new acids,—one having the formula $C_{11}H_{14}O_2$, which we propose to call turmeric acid; the other either $C_{10}H_{12}O_4$ or $C_{10}H_{10}O_4$, to which we would give the name apoturmeric acid.

In order to obtain this product, a little turmerol was allowed to stand at ordinary temperatures with a moderately strong solution of potassic permanganate until the latter was reduced. The operation was carried on in large beakers, and the yield seemed to be better when not more than 500 cc. of permanganate solution were used in each oxidation, than when larger quantities were employed; with this amount the action came to an end in about three days. After the liquid had become colorless, the oxide of manganese and

unaltered oil were removed by filtration, and again treated with permanganate solution; this treatment being repeated until the permanganate ceased to act, when it was found that the oxide of manganese was essentially free from organic matter, and therefore that the entire product was contained in the aqueous filtrate. The mixed filtrates from a number of operations were then concentrated on the water-bath, acidified with sulphuric acid, extracted several times with ether, and the extract, a black tarry liquid, distilled with steam, when a yellow oil (A) passed over with some difficulty; this was mostly turmeric acid. The residue in the flask (B) contained a tarry substance and apoturmeric acid, which not infrequently separated in white crystals as the solution cooled.

Upon distilling with steam the solution left after extraction with ether, it yielded a strongly acid distillate containing a little of the yellow oily acid, from which it was freed in great part by extracting it five times with ether. It was then boiled with baric carbonate to convert it into a barium salt, which crystallised, after it had evaporated spontaneously nearly to dryness; the crystals, freed from mother-liquor by pressure between filter-paper, were nearly pure baric acetate, as shown by the following analysis:

1.1745 grams of the air-dried salt lost 0.0661 gram when dried at 100°.

	Calculated for $Ba(C_2H_3O_2)_2H_2O$.	Found.
Water	6.59	5.63

1.1038 grams of the dried salt gave 0.9974 gram of baric sulphate.

	Calculated for $Ba(C_2H_3O_2)_2$.	Found.
Barium	53.73	53.13

As, however, a solution of the silver salt blackened much more easily than argentic acetate should, and crystallised at first in balls made up of radiating needles, although after one or two recrystallisations attended by blackening it gave the flattened needles characteristic of argentic acetate, we suspected that there might be some other acid present, the barium salt of which had been removed in the mother-liquors, and resorted to fractional acidification with sulphuric acid to settle this point. For this purpose a quantity of the acid distillate, after treatment with ether, was converted into the calcium salt and treated with one-third of the amount of sulphuric acid necessary to set free all the acid it contained; it was then distilled with steam as long as the distillate

showed an acid reaction. The residue in the flask was treated twice successively with the same amounts of sulphuric acid, and the first and third fractional distillates converted into calcium salts.

I. 0.3582 gram of salt from the first fraction gave 0.2894 gram of calcic sulphate.

II. 0.2281 gram of salt from the third fraction gave 0.1980 gram of calcic sulphate.

	Calculated for $Ca(C_2H_3O_2)_2$.	Found. I.	Found. II.	Calculated for $Ca(C_3H_5O_2)_2$.
Calcium	25.32	23.76	25.54	21.50

From these numbers it appears that there is no large amount of any acid except acetic present, and the blackening and different crystalline forms of the silver salt were probably due to a trace of turmeric acid which could not be removed by ether.

As it was possible that a neutral lactone might have been formed, a portion of the acid liquid was boiled with baric carbonate, distilled with steam, and the neutral distillate boiled with baric hydrate for some time; as after removing the baric hydrate with carbonic dioxide there was no residue on evaporation, no lactone was formed.

The formation of carbonic dioxide was determined by a special experiment, in which a portion of turmerol was oxidised out of contact with the air; upon acidifying with sulphuric acid a gas was given off, which gave a copious white precipitate with lime-water.

A. *Study of the Distillate obtained from the Ether Extract with Steam.*

This consisted principally of water, with a few yellow or brown oil-drops floating in it. It was extracted with ether, and the extract, which had acid properties, boiled with water and calcic carbonate. The solution of a calcium salt thus obtained, when allowed to evaporate spontaneously, deposited spherical collections of white needles and a yellow viscous substance somewhat more soluble than the crystals.

The crystalline body proved to be the calcium salt of the new acid, which we have called turmeric acid, after it had been purified by repeated crystallisation from water, which is tedious in the highest degree, as all the solutions and evaporations have to be carried on at ordinary temperatures; in fact, it took us more than a

year and a half to prepare and purify the four or five grams of this substance which have served for the present research.

In regard to the nature of the viscous non-crystalline salt we cannot speak with certainty, as we were unable to obtain it free from calcic turmerate; but we are of the opinion that it is a salt of an isomeric acid, as an analysis of the salt, which had not been purified by crystallisation, gave 8.12 per cent. of calcium instead of 8.93 calculated for calcic turmerate, and the acid set free from the amorphous salt remained liquid even at — 5°, while turmeric acid solidifies at ordinary temperatures.

The total yield of mixed calcium salts cannot be more than one or two per cent. of the turmerol oxidised, and the proportion of amorphous salt in this product is comparatively small.

Turmeric Acid, $C_{11}H_{14}O_3$.—The calcium salt prepared and purified as just described was treated with hydrochloric acid, and then extracted with ether. On evaporating off the ether, a yellowish oil was left, which crystallised on standing, and gave the following analytical results after being dried *in vacuo*:

I. 0.2198 gram of substance gave 0.5954 gram of carbonic dioxide and 0.1586 gram of water.

II. 0.1320 gram gave 0.3584 gram of carbonic dioxide and 0.0960 gram of water.

	Calculated for $C_{11}H_{14}O_3$.	Found. I.	Found. II.
Carbon	74.16	73.87	74.04
Hydrogen	7.86	8.02	8.08

Properties.—The turmeric acid, as at first precipitated, is an oil, which gradually solidifies in long white branching needles, or crystalline masses, with a faint smell like cocoanut; freed from oil by pressing between the filter-paper it melts at 34°–35°; it is slightly soluble in water, very freely in all the other common solvents except methyl alcohol, in which, however, it is readily soluble, so that it was found impossible to crystallise it from this or any other solvent; it distils slowly with steam, and is a monobasic acid. When oxidised with a hot solution of potassic permanganate, not in too great excess, it gives the apoturmeric acid, which will be described later in this paper.

Calcic Turmerate, $Ca(C_{11}H_{13}O_2)_2.3H_2O$.—The preparation and purification of this salt have been described in connection with the manufacture of turmeric acid. For analysis it was dried, at first *in*

vacuo, and afterward at 100° or 110°, when several agreeing analyses gave the percentage of calcium 10.78–11.13, whereas calcic turmerate contains only 10.15 per cent. of calcium. This led us to suspect that the salt had undergone a constant decomposition at this temperature, which we were the more inclined to do, because at first it lost weight very rapidly, but later the loss dropped to a few milligrams a day, and more than a week of continuous heating was necessary to obtain a constant weight, while at the same time the salt gradually became brown and viscous. We have therefore calculated our results upon the salt dried *in vacuo*, and these agree very well with the amount of calcium in calcic turmerate containing three molecules of water of crystallisation.

I. 0.3131 gram of substance dried *in vacuo* gave 0.0970 gram of calcic sulphate.

II. 0.2993 gram gave 0.0912 gram of calcic sulphate.

	Calculated for $Ca(C_{11}H_{13}O_3)_2.3H_2O$.	Found. I.	Found. II.
Calcium	8.93	9.11	8.96

Properties.—It forms spherical collections of white radiating needles looking like chestnut-burrs; the purer the salt the more distinct are the separate needles. When boiled with water it melts to a viscous mass, which is then acted on by the water only very slowly; it is therefore advisable to dissolve it in the cold.

7.861 grams of the solution saturated at 16° gave 0.0344 gram of calcic sulphate. Therefore a saturated solution at 16° contains 1.27 per cent. of $Ca(C_{11}H_{13}O_3)_2$.

The salt is also soluble in alcohol, and is decomposed by a heat of 100°–110°, as already stated.

The behavior of a solution of the calcium salt with various reagents was also studied, and it was found to give a white flocculent precipitate with aluminic chloride; a similar reddish-brown precipitate with ferric chloride; heavy white precipitates with mercurous or plumbic salts, the plumbic salt melting under boiling water, and forming, when prepared in quantity, an uninviting yellowish viscous mass; cupric nitrate produced pale-blue flocks, and argentic nitrate a heavy white precipitate somewhat soluble in water; the other common reagents gave no characteristic precipitates.

An attempt was made to prepare and analyse the *silver salt*, but we did not succeed in purifying it, since its solubility in water is so great that the impurities could not be removed by washing without

using a larger amount of substance than was at our disposal; and it was impossible to recrystallise it from water, as its solutions decomposed with great ease. An imperfectly washed specimen gave a result which approaches that required by theory.

0.1932 gram of the salt dried *in vacuo* gave 0.0750 gram of silver.

	Calculated for $AgC_{11}H_{13}O_2$.	Found.
Silver	37.89	38.82

The *barium salt* resembled the calcium salt in that it formed little balls of radiating needles, but showed a much greater tendency to separate in a viscous state, so that it was hard to obtain it crystallised.

The behavior of the *zinc salt* is very characteristic; when a solution of it is prepared by boiling the acid with water and zincic oxide, allowing the liquid to cool, and filtering, the clear solution thus obtained becomes turbid, when warmed even to temperatures far below the boiling point, but clears up again as the liquid cools. The salt could be obtained only as a viscous mass.

B. *Study of the Residue from Distillation with Steam.*

The flask-residue, after the turmeric acid had been distilled off with steam, contained a black tarry substance, and not infrequently a white crystalline acid, which can be separated from the tar by treatment with boiling water. On extracting with ether the aqueous mother-liquor, from which the white acid had crystallised, a third substance, yellow and buttery, was obtained. All these substances are acids, but we have been unable to bring the black tarry acid or the yellow buttery one into a state fit for analysis, and can only say that the very ill-defined calcium salt of the former contained 1.69 per cent. of calcium, while the latter gave on oxidation an acid melting near 180°, which was not phthalic acid, and was formed in such small quantity that we were unable to determine whether it was a pure substance or only a mixture of apoturmeric acid with some impurity.

Apoturmeric Acid.—The white crystalline acid was separated from its impurities by crystallisation from boiling water, till it showed a constant melting-point. The same acid is obtained by oxidising calcic turmerate with a hot solution of potassic permanganate, and a good part of the substance used for analysis was prepared in this way; the yield, however, was so small, not over

10 per cent. of the turmeric acid used, that we have been unable to determine even its formula with certainty, as will be seen from the following analyses.

0.1138 gram of substance gave 0.2582 gram of carbonic dioxide and 0.0590 gram of water.

	Calculated for $C_{10}H_{10}O_4$.	Found.	Calculated for $C_{10}H_{12}O_4$.
Carbon	61.86	61.87	61.22
Hydrogen	5.15	5.76	6.12

The *calcium salt* made by boiling the acid with calcic carbonate and water gave the following results:

I. 0.2274 gram of salt dried *in vacuo* lost 0.0304 gram when heated to 100°.

II. 0.1390 gram lost 0.0186 gram when heated to 100°.

	Calculated for $CaC_{10}H_8O_4 2H_2O$.	Found. I.	Found. II.	Calculated for $CaC_{10}H_{16}O_4 2H_2O$.
Water	13.43	13.36	13.39	13.33

0.1826 gram gave 0.3370 gram of carbonic dioxide, 0.0758 gram of water, and 0.1016 gram of calcic sulphate.

	Calculated for $CaC_{10}H_8O_4$.	Found.	Calculated for $CaC_{10}H_{10}O_4$.
Carbon	51.72	50.32	51.29
Hydrogen	3.40	4.61	4.27
Calcium	17.24	16.36	17.10

The *barium salt* prepared like the calcium salt gave a result which is not in harmony with the preceding.

0.2704 gram of salt dried at 100° gave 0.1742 gram of baric sulphate.

	Calculated for $BaC_{10}H_8O_4$.	Found.	Calculated for $BaC_{10}H_{10}O_4$.
Barium	41.64	37.87	41.39

If, however, we suppose that the salt retained two molecules of water at 100°, the result agrees very well with the calculated per cents.

	Calculated for $BaC_{10}H_8O_4 2H_2O$.	Found.	Calculated for $BaC_{10}H_{10}O_4 2H_2O$
Barium	37.53	37.87	37.32

But this supposition is, to say the least, improbable, as the calcium salt loses its water easily at 100°; unfortunately, we did not have enough of the acid to repeat the analysis of the barium salt.

Properties.—The apoturmeric acid separates from its solution in boiling water as a white, rather stiff, woolly mass, which renders the whole solid, if the solution was a strong one; it melts at 221°, and is easily soluble in alcohol, ether, and boiling water; nearly insoluble in cold water.

Ammonic apoturmerate is not very freely soluble, and gives the following characteristic precipitates: With plumbic acetate, white flocculent; with cupric sulphate, whitish green,—both soluble in an excess of the precipitant; with mercurous nitrate, white flocks; with ferric chloride, yellowish white; with argentic nitrate, a heavy white precipitate, slightly soluble in boiling water. With the other common reagents it gives no precipitates at all, or very slight white ones.

Several attempts were made to oxidise the apoturmeric acid, but they gave no satisfactory result. The acid was attacked only with difficulty either by potassic permanganate or chromic anhydride, and the only insoluble substance left after the oxidation was simply undecomposed apoturmeric acid. In no case have we observed the formation of terephthalic acid from apoturmeric, or from carefully purified turmeric acid; but this acid has appeared when a calcic turmerate containing the non-crystalline impurity was oxidised. We should therefore ascribe the formation of terephthalic acid from turmerol by violent oxidation rather to this substance than to the turmeric acid formed; but our experiments must be repeated on a larger scale before we can consider this point finally settled.

It is to be regretted that we were unable to settle definitely the composition of the apoturmeric acid, as this would have thrown much light on the constitution of turmeric acid; as it is, it is not worth while to advance any hypotheses on this subject.

We may add one more observation in reference to turmerol, viz. isobutylturmerol does not give an addition-product with bromine, but there is formed with evolution of hydrobromic acid a most uninviting unstable viscous oil.

XXXIX.—ON THE ACTION OF PHOSPHORUS TRICHLORIDE ON ANILINE.

By C. Loring Jackson and A. E. Menke.

The only paper on this subject which we have been able to find was published by Tait in 1865;[1] in it he describes the product of the action of phosphorus trichloride on aniline as a white salve-like mass easily soluble in water, alcohol and ether, which, when freed from an excess of aniline, had the composition $(C_6H_5NH)_3P_3HCl$, gave a chlorplatinate and several double salts, but yielded no satisfactory result when he attempted to set free the base.

We were induced to take up the study of this reaction by the hope that a further investigation of Tait's substance might lead to interesting results; but in this we were disappointed, as we have not succeeded in obtaining it, and, as far as our experiments go, are inclined to think it must have been a mixture instead of a definite compound. At the same time, we cannot state with absolute certainty that it is not present in the product formed when a decided excess of aniline is used, since the impossibility of continuing our work after the beginning of the summer vacation prevented us from making the investigation of this product as thorough as we wished. For the same reason other parts of this research can be published only in a very fragmentary and imperfect condition.

The isolation of the compounds containing phosphorus formed by the action of phosphorus trichloride on aniline, in the proportion of one molecule to three, is surrounded by difficulties which we have found insurmountable; but, in spite of this, our experiments have determined with a fair degree of certainty the nature of these compounds, as will appear from the following general statement of our results, and the argument which can be based upon them.

When aniline is added to phosphorus trichloride in the proportion of three molecules of the former to one of the latter, the product, a variable mixture of aniline chloride and a substance containing phosphorus, gives a clear solution with water or alcohol.

[1] Jahresbericht der Chem. 1865, 411. Instit. 1865, 254.

If, however, this product is heated, a waxy mass is obtained, which is soluble in alcohol; but water throws down from this solution a white precipitate having the formula $(C_6H_5NH)_2PHO$. Of the three most probable products of the reaction of phosphorus trichloride and aniline,

(1) $C_6H_5NHPCl_2$,
(2) $(C_6H_5NH)_2PCl$,
(3) $(C_6H_5NH)_3P$,

only (2) could yield $(C_6H_5NH)_2PHO$ by the action of water or alcohol, and we therefore infer that $(C_6H_5NH)_2PCl$ exists in the product after it has been heated. On the other hand, this substance cannot exist in the original product, as this dissolves in water without residue, whereas $(C_6H_5NH)_2PCl$ is converted by water into the insoluble $(C_6H_5NH)_2PHO$; but it must be formed from one of the constituents of the crude substance during the heating. Of the two probable products of the reaction, (1) and (3), mentioned above, it is hard to see how (3), $(C_6H_5NH)_3P$, by heating with aniline chloride, could be converted into $(C_6H_5NH)_2PCl$, while (1), $C_6H_5NHPCl_2$, could easily undergo this change under these conditions; from which we conclude that $C_6H_5NHPCl_2$ and aniline chloride are the products of the action of aniline on phosphorus trichloride under the conditions mentioned. This conclusion is supported by the fact that alcohol or water acts violently on the original product forming aniline phosphite, and it is highly improbable that $(C_6H_5NH)_3P$ would give such a violent reaction.

The remainder of this paper contains a detailed account of the experiments on which the above conclusions are based, a description of the properties and behavior of the new substance $(C_6H_5NH)_2PHO$, and a somewhat fragmentary account of two crystalline substances formed by boiling the crude product with an excess of aniline, one of which may be a derivative of $(C_6H_5NH)_3P$, although this point needs confirmation by further experiments.

Action of Phosphorus Trichloride on Aniline.

When aniline is added to phosphorus trichloride, the reaction is attended with so much heat, that each drop of the aniline hisses like red-hot iron in water when it touches the trichloride; and, if the substances are mixed in about the proportion of three mole-

cules of aniline to one of the trichloride, the product is a hard white solid, with no trace of the salve-like consistency described by Tait. It was proved to be a mixture by the following analyses of three different preparations, which were freed from an excess of either reagent by washing with ether before analysis.

	I.	II.	III.
Carbon	50.82	54.41	43.59
Hydrogen	6.28	7.07	7.10
Chlorine	19.38	23.15	...
Phosphorus	5.48	2.92	...

In the hope of isolating the phosphorus compound, the action of various solvents on the mass was studied,—of all the common solvents, water, alcohol, methyl alcohol, and acetone were the only ones in which it was not essentially insoluble; but, as we found that acetone dissolves aniline chloride, there was no prospect of achieving the purification of the phosphorus compound by its means, and either water or alcohol decomposed it, giving a clear solution,[1] which, on evaporation, left a viscous residue, apparently composed of chloride and phosphite of aniline, as it deposited crystals of the former after standing for some time, and upon solution in water and addition of plumbic acetate gave a heavy white precipitate, which, freed from plumbic chloride by washing with hot water, was proved to be plumbic phosphite, by the following analysis:

0.6986 gram of the salt gave 0.7380 gram of plumbic sulphate.

	Calculated for $PbHPO_3$.	Found.
Lead	72.13	72.16

From this result it is probable that no anilidophosphorus acid was formed.

From what has been said it appears that the product described above differs from Tait's in consistency, in its solubility in ether, and in composition; but if, instead of fulfilling the conditions given above, the trichloride is added to a large excess of aniline, a substance is obtained which resembles Tait's in its salve-like consistency and the fact that it gives a considerable extract with ether; at the same time we cannot think that it has the composition ascribed to it by him, because our analyses given above show that

[1] When water was used there was sometimes a slight residue of $(C_6H_5NH)_3PHO$.

the substance must contain aniline chloride, and this would not have been removed by mere solution in water, the only purification to which it was submitted by Tait. We may add, that the solid matter apparently extracted by ether was really dissolved in the excess of aniline, as it proved insoluble in ether after the aniline was removed, and, as aniline dissolves aniline chloride, we saw no prospect of purifying the phosphorus compound in this way. If, on the other hand, an excess of phosphorus trichloride was used, the product was a white compact mass, from which a considerable amount of solid matter was extracted with ether; but this was due evidently to its solubility in phosphorus trichloride rather than in ether, and, as it contained only two per cent. of phosphorus, it was not thought worth while to pursue this part of the subject further.

Action of Heat on the Original Product.

If the mixture, analyses of which were given above, is heated, it turns orange-red, and gives off aniline chloride, the purity of which was determined by analysis, and a small quantity of a phosphorescent gas, probably phosphoretted hydrogen. This change takes place slowly and partially even at 100°, much more rapidly and completely at 150°, or at even higher temperatures. We usually heated the mass in a porcelain dish over a free flame, regulating the temperature so that aniline chloride sublimed off freely, but no spontaneously inflammable phosphoretted hydrogen was given off. The product when heated with alcohol gave a colorless solution, and a residue of an orange or red color, according to the length of time it had been heated. As this residue was insoluble in all solvents, and could not be purified completely by washing, we are in doubt as to its precise nature; but, as one preparation contained as much as 81.73 per cent. of phosphorus, it cannot be an organic compound, but is either amorphous phosphorus, or the red oxide or solid hydride of that element. The alcoholic solution when treated with water gave a white precipitate of $(C_6H_5NH)_2PHO$, while aniline chloride and phosphite were left in solution, with, so far as we could find, no other substances. The formation of the red body is not essential to the production of the mother-substance of $(C_6H_5NH)_2PHO$, as we obtained, by short heating in a dry test-tube, a yellowish waxy mass, which dissolved completely in alcohol and yielded a large amount of $(C_6H_5NH)_2PHO$ on addition of water; upon longer heating, however, the yellowish substance turned orange-red.

Before going to the description of the phosphorus anilid $(C_6H_5NH)_3PHO$, we may add, that we tried to obtain the chlorine compound from which it is formed by treating the freshly heated orange mass with benzol or with absolute ether, as these solvents seemed to offer the best chance of success. The amount extracted in either case was extremely small, and possessed the most unpromising properties, the ether extract containing lumps of ordinary phosphorus imbedded in a viscous mass, while the benzol extract resembled semi-liquid paint, and gave no evidence that it was a homogeneous compound; it was analysed, however, and contained 5.12 per cent. of chlorine and 21.27 per cent. of phosphorus, whereas $(C_6H_5NH)_3PCl$ requires 14.17 per cent. of chloride and 12.37 of phosphorus.

Phosphorus Anilid, $(C_6H_5NH)_3PHO$.

The preparation of this substance has been just described. In order to purify it, as it did not crystallise, the crude precipitate was redissolved in a little alcohol, and precipitated with water; the viscous mass thus obtained was kneaded thoroughly with water, dissolved again in alcohol, and once more precipitated and washed with water; it was then dried at about 50°, and its composition determined by the following analyses of a number of different preparations:

I. 0.3488 gram of substance gave 0.7992 gram of carbonic dioxide and 0.1918 gram of water.

II. 0.2856 gram gave 0.6502 gram of carbonic dioxide and 0.1610 gram of water.

III. 0.2190 gram gave 0.5012 gram of carbonic dioxide and 0.1180 gram of water.[1]

IV. 0.3402 gram gave after treatment, according to Carius, 0.1590 gram of magnesic pyrophosphate.

V. 0.2016 gram gave 0.0976 gram of magnesic pyrophosphate.

VI. 0.4623 gram gave 49.9 cc. of nitrogen at a temperature of 25° and pressure 766 mm.

	Calculated for $(C_6H_5NH)_3PHO$.	Found. I.	II.	III.	IV.	V.	VI.
Carbon	62.07	62.47	62.04	62.41	...	...	...
Hydrogen	5.60	6.10	6.26	5.99	...	...	...
Phosphorus	13.36	...	...	...	13.05	13.52	...
Nitrogen	12.07	...	...	...	...	...	12.13

[1] We found it best to carry on the combustions in a closed tube, the substance being mixed with oxide of copper, as, if burnt in a boat in oxygen, the carbon was apt to come low, since the fused phosphoric acid prevented the complete combustion of the substance.

Properties.—It forms a white amorphous mass which melts at 87°; all our attempts to obtain it in crystals have been unsuccessful; it is freely soluble in cold alcohol and in ether, insoluble in cold water, but melts under boiling water, and perhaps dissolves to a very slight extent. It is a perfectly neutral body, neither acids nor alkalies affecting it in the cold; even alcoholic sodic hydrate or sodic ethylate acts on it with difficulty; on the other hand, fuming hydrochloric acid, when boiled with it for twelve hours, decomposes it completely into aniline chloride, phosphoric acid, and a small quantity of carbonaceous substance. The formation of the aniline chloride was proved by an analysis of the sublimate, 0.2776 gram giving 0.3114 gram of argentic chloride,

	Calculated for $C_6H_5NH_3Cl$.	Found.
Chlorine	27.41	27.74

the formation of phosphoric acid by qualitative tests with argentic nitrate and ammonic molybdate.

Action of Nitric Acid.—When the substance is gently heated with fuming nitric acid it forms a red solution, from which water precipitates a red resinous body which contains phosphorus, but was not studied further, as the quantity was not large, and its properties were uninviting. By far the principal products of the reaction were contained in the aqueous solution, which left on evaporation yellow crystals having acid properties, and easily characterised by their appearance and melting-point, 120°, as picric acid. Another preparation yielded instead of picric acid the unsymmetrical metadinitrophenol, melting at 113°–115°. These results can be explained by supposing that the nitric acid saponifies the anilid, forming aniline nitrate and phosphoric acid, and the former is afterwards converted into the nitrophenols by the combined action of nitrous and nitric acids.

Action of Acetic Anhydride.—If phosphorus anilid is heated with acetic anhydride and fused sodic acetate on the water-bath, and the product extracted with ether, a viscous mass is obtained, which gradually becomes partially converted into crystals free from phosphorus, melting at 112° after recrystallisation from water, and therefore acetanilid.

From all the observations described above it appears that the substance behaves like an anilid of phosphorus acid.

Action of an Excess of Aniline on the Original Product.

If the immediate product of the action of phosphorus trichloride and aniline, or this product after it has been heated, is boiled for some time with an excess of aniline, there results a mixture of various substances from which we have succeeded in isolating the orange-red substance and phosphorus anilid already described, chloride and phosphite of aniline, and a crystalline substance melting at 208°. There seems to be also a substance with a higher melting-point, and on one occasion a body melting at 150° was obtained; unfortunately we were obliged to break off work on this part of the subject before we had done more than analyse the two substances melting at 208° and 150° respectively, so that we have as yet no satisfactory data for determining their constitution, and also have been able to make no exhaustive search for other products.

Substance melting at 208°.—This compound is obtained from the mixed products of the reaction by washing out the soluble salts with water, extracting the residue with hot alcohol, and purifying the extract by crystallisation from alcohol, till it shows a constant melting-point. It was dried at 100° and analysed.

I. 0.3352 gram gave 0.8032 gram of carbonic dioxide and 0.1770 gram of water.

II. 0.2946 gram gave 0.7047 gram of carbonic dioxide and 0.1520 gram of water.

III. 0.2528 gram gave 0.1200 gram of magnesic pyrophosphate.

IV. 0.2492 gram gave 0.1200 gram of magnesic pyrophosphate.

V. 0.3424 gram gave 40.44 cc. of nitrogen at a temperature of 20.5° and a pressure of 757.3 mm.

	I.	II.	III.	IV.	V.	Mean.
Carbon	65.34	65.24	...	...	...	65.29
Hydrogen	5.86	5.73	...	...	...	5.79
Phosphorus	...	...	13.25	13.47	...	13.36
Nitrogen	...	...	...	...	13.38	13.38

These results agree most nearly with the formula $(C_6H_5NH)_8P_4OH_2$, but are not far removed from $(C_6H_5NH)_7P_3O_2H_2$, as is shown by the following comparison:

	Calculated for $(C_6H_6N)_8P_4OH_2$.	Mean of analytical results.	Calculated for $(C_6H_6N)_7P_3O_2H_2$.
Carbon	65.61	65.29	65.37
Hydrogen	5.71	5.79	5.70
Phosphorus	14.12	13.36	12.06
Nitrogen	12.75	13.38	12.71

According to the first of these formulas the substance would be a derivative of the red oxide or hydrate of phosphorus, while the second can be developed into $[(C_6H_5NH)_3P]_2H_2O_2PC_6H_5NH$; it is possible, therefore, that a study of the decomposition-products of the substance might throw light on its composition. With this view we heated some of it to 140° in a sealed tube with hydrochloric acid and obtained phosphorus and phosphoric acids, aniline chloride, some carbon, and an odor of phenol, but no red product; we have also found that boiling aniline with the red substance, so often mentioned, does not give this compound melting at 208°, so that our results are in favor of the second formula so far as they go, but need revision before much weight can be given to them.

Properties.—The substance crystallises in small white prisms apparently of the monoclinic system, or in long radiating needles with, as far as we could determine, the same melting-point and composition as the prisms; it melts at 208°, and is insoluble in water, freely soluble in hot alcohol, less so in cold, essentially insoluble in ether. Potassic hydrate in aqueous solution does not act on it at first, but gradually decomposes it if the two are boiled together; sulphuric acid acts in the same way; the decomposition with hydrochloric acid has been described already.

Substance melting at 150°.—This compound was obtained at the very end of the term in an attempt to prepare more of the substance melting at 208°; on this account we cannot give the conditions which determine its formation, or anything more concerning it than the following analyses:

0.3492 gram of substance gave 0.7122 gram of carbonic dioxide and 0.2004 gram of water.

0.2562 gram gave, according to Carius, 0.1330 gram of argentic chloride and 0.0890 gram of magnesic pyrophosphate.

	Found.
Carbon	55.62
Hydrogen	6.37
Chlorine	12.83
Phosphorus	9.70

It would not be worth while to attempt to determine the formula of this substance until these results have been tested by further analysis. It crystallises in rather thick white radiating needles, melts at 150°, and resembles the preceding substance in a general way in its solubility.

At no distant date we hope to be able to return to the study of this subject in order to determine the nature of the two substances just described, to investigate more thoroughly the products of the reaction, which are soluble in water, and to take up the compounds formed by aniline and phosphorus trichloride in presence of diluents, which, according to a preliminary experiment, promise to be of great interest.

A NEW HYDROUS MANGANOUS ALUMINIC SULPHATE FROM SEVIER CO., TENN.

By W. G. Brown.

This mineral, which is found in large quantity at the Alum Cave, Sevier Co., Tenn., was described by Troost in the Geological Survey of Tennessee, and after him by Safford in his Geology of Tennessee,[1] as a double sulphate of alumina and potash; and under the head of Kalinite in Dana's System of Mineralogy, Alum Cave is given as one of the localities of its occurrence. The Alum Cave is situated at the head-waters of the Little Pigeon, a tributary of the Tennessee River. Called a "cave," it is an overhanging cliff 80 or 100 feet high and about 300 feet long, the top of which projects some twenty or thirty feet beyond the base. In this sheltered ground the "alum" has collected. Hunters who occasionally visit the cave say there is usually a spring flowing. The rock forming the cliff is a weathered schist containing visible specks of pyrite. In the earth produced by the weathering, at the base of the cliff, the alum is found, not on the surface, but covered by a layer of earth and scattered through it in pieces of various sizes. Epsomite is also found in quantity, and Melanterite sparingly at this locality. The "alum" is used by the country people for dyeing their homespun a reddish-brown, and by them preferred to the commercial alum because of the darker red it gives.

The specimen, a portion of which was taken for analysis, consisted of an irregular compact mass, in the cavities of which the

[1] Geology of Tennessee, 191, 197, 503.

mineral was found in very fine, transparent needles having a decided silky lustre. An optical examination seemed to indicate that the crystallisation was monoclinic. The compact mineral is white, with a faint tinge of rose, pale green or yellow. Lustre waxy or vitreous. Translucent. On exposure to the air effloresces and becomes coated with a basic salt of iron. Hardness 1.5. Specific gravity, taken in alcohol, 1.782 (average of two pieces respectively 1.775 and 1.790). Heated gently in a closed tube gives off water having an acid reaction. Heated strongly, sulphuric acid is liberated. On platinum before the blowpipe, glows intensely, increases in bulk, and turns reddish-brown. The alumina reaction with cobalt nitrate is obscured by this darkening, but can be obtained by heating in a closed tube. Heated with sodium carbonate on platinum, it gives readily the reaction for manganese. Easily soluble in water. The solution is strongly acid and has a sour, astringent-bitter taste.

The analysis was made by the ordinary methods, except that the water was determined by prolonged heating in a covered platinum crucible (to prevent oxidation of the manganous oxide, which did not take place), in an air-bath, at 220°–240° C. and finally at 300° C. As at this temperature some sulphuric acid was driven off, the dried mass was taken and the amount of sulphuric acid in it determined. The difference between this percentage and that obtained from the air-dry mineral was subtracted from the percentage of loss on heating and the remainder taken as the percentage of water.

The results were as follows:

Al_2O_3	=	10.0318
MnO	=	8.7279
FeO	=	.3874
MgO	=	.2998
(CoNi)O	=	.2948
CuO	=	.0168
SO_3	=	35.4723
H_2O	=	44.7756
Insoluble	=	.0650
		100.0714

This leads to the general formula

$$R_2''Al_4(SO_4)_9(H_2O)_{51}$$

where R″ is principally Mn″, with Fe″, Mg, Co, Ni, and Cu″. This formula, assuming R″ to be Mn″ alone, gives the following calculated composition:

$Al_2O_3 = 9.927$
$MnO = 10.365$
$SO_3 = 35.036$
$H_2O = 44.672$

100.000

A comparison of the composition of this mineral with Apjohnite and Bosjemanite[1] led to a recalculation of the formulae as given in Dana, with the result that the minerals from S. Africa have a composition expressed nearly by the formula

$$R''Al_2(SO_4)_4(H_2O)_{21};$$

that from Switzerland by

$$R''_3Al_4(SO_4)_9(H_2O)_{48},$$

and that from Utah a formula which (in the ratio of H_2O) approaches the Tennessee mineral.

This is shown in the following table, where the compositions and ratios are given, and where the analysis of a "Native Ferrous and Aluminic Sulphate from Tepeji," Mexico,[2] has been added:

1. Apjohnite, Lagoa Bay, South Africa. Analyst, Apjohn.
2. Bosjemanite, Bosjeman River, South Africa. Analyst, Stromeyer.
3. Bosjemanite, Salt Lake, Utah. Analyst, Smith.
4. Bosjemanite, Maderan Valley, Switzerland. Analyst, Schweizer.
5.[3] Tepeji, Mexico. Analyst, Lippitt.
6. Sevier County, Tenn.

	1.	2.	3.	4.	5.	6.
Al_2O_3	10.65	11.515	10.40	10.55	9.29	10.0318
Fe_2O_3			0.15			
MgO	0.36	3.690	5.94	3 74		.2998
MnO	6.60	2.167	2.12	2.51		8.7279
FeO				1.06	10.03	.3874
(CoNi)O						.2948
CuO				0.22		.0168
CaO				0.27		
K_2O			.20	0.58		
KCl		.205				
SO_3	33.51	36.770	35.85	35.96	33.75	35.4723
H_2O	48.15	45.739	46.00	44.26	43.13	44.7756
$CaSO_4 + 2H_2O$					2.24	
	99.27	100.086	100.66	99.15	98.44	100.0064

[1] Dana. A System of Mineralogy. 5th Ed. 1870, 653, 654.
[2] Lippitt, Chem. News, **48**, 98.
[3] Changed in form for the sake of comparison.

Ratios.	1.			2.			3.		
Al_2O_3	.104	= 1.02		.112	= 1.00		.101	.102 =	1.00
Fe_2O_3							.001		
MgO	.009	.102 =	1.00	.092			.148		
MnO	.093			.030			.030		
FeO									
(CoNi)O					.123 =	1.08		.18 =	1.76
CuO									
CaO									
K_2O				.001			.002		
SO_3	.419	= 4.1		.459	= 4.09		.448	=	4.39
H_2O	2.675	= 26.22		2.451	= 22.69		2.555	=	25.04

Ratios.	4.			5.			6.		
Al_2O_3	.103	= 1.00		0.91	= 1.00		.098	=	1.00
Fe_2O_3									
MgO	.093						.007		
MnO	.035						.123		
FeO	.015			.139	= 1.53		.005	.14 =	1.43
(CoNi)O		.157 =	1.53				.004		
CuO	.003								
CaO	.005								
K_2O	.006								
SO_3	.449	= 4.35		.422	= 4.63		.443	=	4.51
H_2O	2.459	= 23.78		2.396	= 26.33		2.488	=	25.39

These form two well-marked groups:

		Al_2O_3.	R″O.	SO_3.	H_2O.	
a.	1.	1.02	1.00	4.10	26.22	$R''Al_2(SO_4)_4(H_2O)_{24}$
	2.	1.00	1.08	4.09	22.69	
b.	3.	1.00	1.76	4.39	25.04	$R''_3Al_4(SO_4)_9(H_2O)_{51}$
	4.	1.00	1.53	4.35	23.78	
	5.	1.00	1.53	4.63	26.33	
	6.	1.00	1.43	4.51	25.39	

Neglecting the water, the ratio of R″O to Al_2O_3 is in *a*, 1 : 1; in *b*, 3 : 2.

The two minerals in group *a* differ, in that Apjohnite is a manganous aluminic sulphate, and the African Bosjemanite a manganous magnesic aluminic sulphate.

The minerals in group *b* are of three kinds:

1. Those from Utah and Switzerland are manganous magnesic aluminic sulphates with an excess of magnesia over manganous oxide; this is also the case with the African Bosjemanite.

2. The ferrous aluminic sulphate from Mexico.
3. The manganous aluminic sulphate from Tennessee.

Whether these differences in composition are sufficient to warrant the giving of specific names to these compounds the writer does not feel competent to decide.

UNIVERSITY OF VIRGINIA, *February* 7, 1884.

ON SOME NEW FORMS OF ALBUMOSE.

BY W. KÜHNE AND R. H. CHITTENDEN.

(*Concluded from p.* 50.)

III. *Heteroalbumose.*

During dialysis, particularly of the first protalbumose solution with its abundance of sodium chloride, heteroalbumose separates out in the manner already mentioned, always gummy and thus usually more or less adherent to the sides of the parchment paper, so that frequently even large quantities may be overlooked unless the tubes are cut open. At first the body takes on that turbid, soapy-water-like condition, in the protalbumose solution, so often seen in impure solutions of hemialbumose, and which cannot be removed by filtration; later a syrupy layer forms from this emulsion, which spreads itself out partly in thick lumps and partly as a uniform varnish on the surface of the fluid, appearing as a granular sediment only when in large quantities. By continued withdrawal of the salt all of these forms become more compact and viscous, but only a little more opaque; and the mass, on being scraped out with a spatula and rubbed up with water, still remains transparent, without inclining to separate into flocks. The substance cannot therefore be readily collected on a filter; the fluid is simply decanted and the remainder of the wash-water allowed to drain off by simply inverting the dish. The heteroalbumose then dries in the form of glassy, brittle pieces, not differing in appearance from gelatin tablets, which in the impure condition are tinged with

yellowish or brown and even bright violet, but after purification are as colorless as the purest glass. Unlike gelatin, however, the pieces flake off easily from the glass and porcelain upon which they are dried.

There are two methods of purification: solution in 5–10 per cent. sodium chloride and precipitation with rock salt, re-solution in salt water and dialysis, or simple dialysis of the first filtered salt solution. By the first method there is considerable loss, since the precipitate produced by the salt is not wholly soluble again in dilute salt solutions. The sodium chloride precipitate is gelatinous and elastic, similar to myosin when precipitated by salt. In pure water heteroalbumose is insoluble; the pieces simply become soft and swell up without falling apart, and when the mixture is filtered, even after standing several days, the fluid gives no indications of albumose with the xanthoprotein reaction. A similar result is also obtained when the substance is boiled with water, though the albumose itself becomes more opaque. Sodium chloride solutions from under 0.5 per cent. to saturation dissolve heteroalbumose, quite slowly, it is true, but still in considerable quantity, the best results apparently being obtained with solutions containing from 5 to 10 per cent. of salt. Solutions rich in heteroalbumose are rendered quite turbid by the addition of water. Excess of salt in substance produces an abundant precipitate, as before mentioned, but the separation is never complete, and thus considerable unaltered heteroalbumose can be obtained by the dialysis of the filtrates. Solid heteroalbumose certainly swells up somewhat in water and softens to an almost syrupy mass, without, however, becoming so voluminous as gelatin, for example; when, however, 10 per cent. salt solution is poured over it, heteroalbumose swells up very noticeably and is partially dissolved. If when in this condition pure water is poured over it and the water several times carefully renewed, the very transparent mass contracts and becomes opaque like dull glass.

In addition to neutral salt solutions, dilute acids, alkalies and alkaline carbonates are good solvents for heteroalbumose. Solutions made with the aid of the latter reagents are in general precipitated by neutralisation, never, however, completely, and as a rule the completeness of this precipitation is directly dependent upon the amount of salt formed by neutralisation; the greater the amount of salt the less complete being the precipitation.

Coagulation of Heteroalbumose.

Nothing characterises heteroalbumose more than its alteration by boiling and the properties of the coagulum thus formed. Suspended in water, thereby becoming somewhat swollen, the substance is coagulated by heat after the manner of many undissolved albuminous bodies; for not only do the pieces of the albumose become shrunken and opaque, but they also become wholly insoluble in solutions of sodium chloride of all degrees of concentration. The appearance of the coagulum is quite peculiar; during the heating the substance apparently melts, so that it sticks in strings and patches to the sides of the glass, which after cooling solidify to a resinous or leather-like mass. In solution heteroalbumose likewise coagulates, even in the presence of the weak but still noticeable alkaline reaction which is characteristic of the solution in sodium chloride.

This coagulation is without doubt dependent upon the proportion of the albumose to the sodium chloride used, less so upon the concentration of the salt, for we saw 0.5, 2, 3 and 5 per cent. sodium chloride solutions coagulate by heat with almost equal distinctness, when they were not nearly saturated with albumose; while, on the other hand, when previously diluted with three to five times their volume of sodium chloride solution of like concentration, the solutions would remain perfectly clear on boiling and even afterwards on cooling.

If the proportion is made different, on warming the solution a transitory turbidity is noticed, which by boiling disappears, and on cooling reappears somewhat intensified; on increasing the content of albumose in the solution, the turbidity at 100° C. becomes permanent to such an extent, at least, that the boiling fluid appears milky, and on cooling a slight flocculent precipitate makes its appearance. The hot fluid scarcely passes at all through filter paper, but as the emulsion becomes cool and a flocculent precipitate forms, a quantity of moderately clear fluid filters through sufficient to prove by means of the nitric acid reaction that the coagulation is quite incomplete. Moreover, with the non-coagulated portion of the substance there is as little alteration to be found as in the substance boiled with an excess of salt solution, in which, as before mentioned, there are no appearances whatever of coagulation.

Solutions of heteroalbumose rendered non-coagulable by the presence of a sufficient excess of salt, become by the gradual addi-

tion of acetic acid more and more turbid, until finally they again become clear; a similar reaction is obtained with nitric acid, which, in slight excess, even in the cold colors the solution yellow. Solutions once made clear in this manner by either acetic or nitric acid, remain so on boiling and also on cooling; precipitation however can be produced by the addition of stronger salt solution in the cold, but as the mixture is heated the solution becomes nearly clear, growing turbid again when cold.

Addition of nitric or acetic acid in such quantity that a noticeable turbidity ensues is followed on warming by an increase of the same, which disappears at the boiling point, but returns again considerably increased on cooling.

Properties of Coagulated Heteroalbumose.

We have studied these reactions principally with the substance obtained by boiling heteroalbumose suspended in water, since the substance separating from a salt solution after boiling and then cooling cannot be conveniently collected on a filter, on account of its becoming so finely emulsionised by the melting at 100° C.

Heteroalbumose coagulated by boiling dissolves gradually, but at the same time completely, in hydrochloric acid of from 0.1 to 0.2 per cent., solution being preceded by a swelling up of the substance. It is but very slightly soluble in sodium carbonate of 0.25 to 3.0 per cent., only very faint albumose reactions being obtained in the filtrates with nitric acid. Once dissolved in dilute acids, the coagulum is completely changed, being reconverted in great part into genuine heteroalbumose, while the remaining portion is changed into a substance which agrees perfectly with dysalbumose. Thus the acid solution gives on neutralisation a precipitate which dissolves immediately in dilute sodium carbonate, in part even in sodium chloride of 0.5 to 5.0 per cent., so that precipitation produced in this manner by neutralisation is never complete, owing to the sodium chloride formed. That which remained dissolved in the neutral fluid, together with that which was taken up from the neutralisation precipitate by washing with sodium chloride, behaved in every respect, so far as we could see, like the original heteroalbumose, and which we were able by long-continued dialysis to again separate therefrom; only there was always noticed a portion insoluble in sodium chloride and which was dissolved only by dilute acids or sodium carbonate, the dysalbumose.

That heteroalbumose coagulated from salt solutions does not differ from the coagulum formed by boiling with water is manifest from the continued milkiness of the sample after the addition of sodium carbonate, and also from the clearing up of the fluid by dilute hydrochloric acid, after which alkaline carbonates produce at first a precipitate, which disappears, however, on the addition of an excess of the alkali.

Formation of Albumosat.

If a nearly saturated solution of heteroalbumose in sodium chloride of 3 to 4 per cent. is mixed drop by drop with concentrated hydrochloric acid as long as the precipitate formed at first is dissolved by agitation, or treated in a similar manner with concentrated sodium hydroxide, in which case no precipitation takes place, solutions are obtained which are precipitated by neutralisation after the manner of albuminates. In both cases separation of the precipitate commences a little before the neutralisation point is reached, and appears to be ended when the solution is exactly neutral. The precipitations are, however, never complete, and in comparison with the portion of substance remaining dissolved in the neutral salt solution are quite unimportant.

Boiling genuine heteroalbumose with dilute sodium carbonate or with 0.2 per cent. hydrochloric acid yields solutions of no different proportions than the same solvents give at ordinary temperatures.

Strong acids and alkalies produce on heteroalbumose, to a limited extent, a change similar to the change produced in coagulation, as in the formation of albuminates from undecomposed albumin.

Reactions of Heteroalbumose.

Acetic acid and potassium ferrocyanide produce a heavy turbidity, completely soluble in excess of acetic acid. If a solution of heteroalbumose be mixed with so much acetic acid that the fluid remains clear in the cold, and then a single drop of ferrocyanide be added, which renders the fluid quite turbid, and this followed by the further addition of 20 per cent. acetic acid until the turbidity becomes somewhat lightened, the application of heat then causes the turbidity to almost completely disappear, returning, however, greatly increased as the fluid cools.

With sodium hydroxide and cupric sulphate heteroalbumose gives the so-called biuret reaction; a very slight excess of copper,

however, is sufficient to completely hide this reaction, so that only the blue-violet of the albumin is to be recognised.

By boiling with lead acetate and sodium hydroxide the brown color produced appears less distinct than would be expected from the content of the solution in sulphur-containing material.

Cupric sulphate, neutral and basic lead acetate produce heavy precipitates in the sodium chloride solution of heteroalbumose; the precipitates are insoluble in excess of the reagents.

Towards mercuric chloride heteroalbumose acts very differently than the prot- and dysalbumose, inasmuch as it is not rendered at all turbid even in alkaline, neutralised or faintly acid solutions by either a moderate or excessive addition of the mercury salt. On the addition of acetic acid, however, a heavy precipitate is produced, which is soluble only in a large excess of glacial acetic acid. A solution of heteroalbumose mixed with acetic acid until the solution, at first turbid, has become clear again, is precipitated by an excess of mercuric chloride.

For analysis a preparation (*H*) was used, which had been twice precipitated by dialysis, and while still moist treated with alcohol and ether. When dry it appeared as a fine powder, slightly grey in color.

Heteroalbumose H.

I. 0.5318 gram gave 0.3167 gram H_2O = 6.61 per cent. H and 0.9790 gram CO_2 = 50.20 per cent. C.

II. 0.7977 gram gave 0.4760 gram H_2O = 6.63 per cent. H and 1.4700 grams CO_2 = 50.25 per cent. C.

III. 0.5731 gram gave 0.3473 gram H_2O = 6.73 per cent. H and 1.0598 grams CO_2 = 50.42 per cent. C.

IV. 0.5113 gram gave 73.92 cc. N at 19.2° C. and 761.6 mm. pressure = 0.0869289 gram N = 17.00 per cent.

V. 0.5407 gram gave 77.93 cc. N at 19.9° C. and 765.37 mm. pressure = 0.0918370 gram N = 16.98 per cent.

VI. 0.4545 gram gave 0.0041 gram ash = 0.90 per cent.

VII. 0.7010 gram gave 0.0064 gram ash = 0.91 per cent.

The ash was composed entirely of gypsum.

The ash from 1.1555 grams substance gave 0.0033 gram $BaSO_4$ = 0.03 per cent. S, contained in the original substance as gypsum.

VIII. 0.5448 gram substance gave after the nitrate fusion 0.0472 gram $BaSO_4$ = 1.18 per cent. S; deducting 0.03 per cent. = 1.15 per cent. S.

IX. 0.3085 gram gave after the nitrate fusion 0.0265 gram $BaSO_4$ = 1.17 per cent. S; deducting 0.03 per cent. = 1.14 per cent. S.

Percentage composition of ash-free heteroalbumose *H*:

								Average.
C	50.64	50.70	50.88	...	...	...	...	50.74
H	6.67	6.69	6.79	...	...	...	...	6.72
N	...	...	...	17.15	17.13	...	...	17.14
S	...	...	...	...	...	1.17	1.16	1.16
O	...	...	...	...	...	...	...	24.24

To obtain the specific rotary power, 0.9700 gram dry substance = 0.9613 gram ash-free substance was dissolved in 35 cc. H_2O + 20 cc. 0.2 per cent. HCl, in which 1 cc. contained 0.017478 gram pure substance. As a mean of 3 observations the solution in a 100 mm. tube rotated the light 1.2° to the left, therefore,

$$(\alpha)_D = \frac{1.2^\circ}{0.017478 \cdot 1} = -68.65^\circ.$$

IV. *Dysalbumose.*

This body is obtained by careful extraction of the insoluble residue remaining from the treatment of Witte's "pepton" with salt solution. The residue is first extracted with saturated, then with 10 and 5 per cent. salt solutions, and finally with water. It is then treated with 0.2 per cent. hydrochloric acid, by which nearly all is dissolved, filtered, and the filtrate made exactly neutral. So large a portion has now become soluble in sodium chloride that by dialysis of the filtrate, together with the wash fluid which at first consisted of 5 per cent. sodium chloride, a considerable quantity of albumose is obtained, which behaves exactly like heteroalbumose. The portion not changed into heteroalbumose is, after thorough washing with sodium chloride and water, for which purpose it is repeatedly rubbed up fine, extracted with alcohol and ether.

Analysis of the so-obtained light grey powder (preparation *J*) gave the following results:

Dysalbumose J.

I. 0.5086 gram gave 0.3141 gram H_2O = 6.86 per cent. H and 0.9384 gram CO_2 = 50.31 per cent. C.

II. 0.5438 gram gave 0.3299 gram H_2O = 6.73 per cent. H and 0.9997 gram CO_2 = 50.13 per cent. C.

III. 0.4068 gram gave 0.2500 gram H_2O = 6.83 per cent. H and 0.7501 gram CO_2 = 50.28 per cent. C.

IV. 0.4437 gram gave 62.93 cc. N at 18.6° C. and 768.21 mm. pressure = 0.0748023 gram N = 16.86 per cent.

V. 0.6524 gram gave 94.16 cc. N at 19.6° C. and 758.4 mm. pressure = 0.1101142 gram N = 16.87 per cent.

VI. 0.6914 gram gave 0.0088 gram ash = 1.27 per cent.

VII. 0.7030 gram gave 0.0090 gram ash = 1.28 per cent.

The ash contained no carbonic acid, only some ferric oxide and calcium sulphate.

The ash from 1.3944 grams substance gave 0.0031 gram $BaSO_4$ = 0.03 per cent. S, in the original substance in the form of sulphate.

VIII. 0.5400 gram substance gave by the nitrate fusion 0.0509 gram $BaSO_4$ = 1.29 per cent. S; deducting 0.03 per cent. = 1.26 per cent. S.

IX. 0.5480 gram gave after the nitrate fusion 0.0480 gram $BaSO_4$ = 1.20 per cent. S; deducting 0.03 per cent. = 1.17 per cent. S.

Percentage composition of ash-free dysalbumose *J*:

								Average.
C	50.95	50.77	50.92	...	...	...	...	50.88
H	6.95	6.82	6.92	...	...	...	...	6.89
N	...	...	...	17.07	17.08	...	...	17.08
S	...	...	...	...	...	1.28	1.19	1.23
O	...	...	...	...	...	...	...	23.92

The specific rotary power could not be satisfactorily determined, owing to the deep color of the solution.

Dysalbumose, as is plainly seen, does not differ materially in composition from the other forms of albumose, certainly not more than these differ from each other; while, like the other forms of albumose, it differs very decidedly from the albumins, syntonins, etc.; which fact is alone sufficient to remove the suspicion that the substance belongs to a residue of non-separated neutralisation precipitate (Meissners), or the so-called digestion syntonin. Further, this idea is completely overthrown by the ready conversion of our preparation into heteroalbumose. It is only necessary to dissolve some of it in 1 per cent. sodium carbonate, when on neutralisation it

will be found (with the exception of a hardly noticeable residue) quite soluble in sodium chloride, and can then be easily obtained by dialysis, with all the properties of heteroalbumose. We therefore consider dysalbumose simply as a form of heteroalbumose, which has become insoluble in neutral salt solution, and thus its origin, by treatment of the digestive solutions with salt, is readily comprehended, since pure heteroalbumose cannot be precipitated by salt without being partially converted into a substance not distinguishable from dysalbumose. Heteroalbumose likewise suffers the same change by long preservation under alcohol or in a dry condition; for the preparations, at first completely soluble in sodium chloride, become after a time more or less insoluble, so that a residue remains which at the best forms with salt water only a milky emulsion.

As to the reactions of dysalbumose, it is only necessary to refer to heteroalbumose, since in both acid and alkaline solutions of the former we found nothing characteristic, other than the solubility of the nitric acid precipitates by heat and their reappearance on cooling; with dysalbumose which had become soluble in salt solutions, no other reactions were observed than those described under heteroalbumose.

While the several forms of albumose just described are seen to differ somewhat in their general properties, the percentage composition of the various products shows a remarkable degree of uniformity. This close agreement in composition, which is plainly apparent from the following table, is probably due in great part to the purity of our preparations, which were not only carefully prepared, but were made in large quantities, thus admitting of even lavish purification. In the table the averages of the individual analyses are given, calculated on the ash-free substance, while for the sake of comparison the content of ash is given, also the specific rotary power[1] as determined in very dilute hydrochloric acid solutions (under 0.1 per cent.).

[1] The figures for specific rotary power agree with the statement of Salkowski (*loc. cit.* p. 213), "about $-75°$" for the aqueous solution of his substance, which probably consisted mainly of prot- and deuteroalbumose.

	Protalbumose.			Protalbumose. NaCl P. P. Acid P. P.		Deuteroalbumose.		Hetero-albumose.	Dys-albumose.
	A.	*B.*	*C.*	*D.*	*E.*	*F.*	*G.*	*H.*	*J.*
C	50.89	50.39	50.54	51.50	50.55	50.47	50.84	50.74	50.88
H	6.83	6.74	6.69	6.80	6.85	6.81	6.85	6.72	6.89
N	17.12	17.12	17.34	17.13	17.01	17.20	17.14	17.14	17.08
S	1.17	1.07	1.17	0.94	1.07	0.87	1.07	1.16	1.23
O	23.99	24.68	24.26	23.63	24.52	24.65	24.10	24.24	23.92
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Ash	0.90	0.22	2.58	1.60	1.32	1.77	0.68	0.90	1.27
$(a)_D$	−72.64°	−79.05°	−77.90°	−73.18°	−71.40°	−74.41°	−79.11°	−68.65°	...

V. *Albumose in Urine in Osteomalachia.*

Of this substance we had for examination only a small residue of the dry, preserved material precipitated by alcohol from the urine of a patient with the above disease, a description of which was given in our previous article.[1] In spite of the rarity of the object it seemed worth the labor to use some of the substance for the purpose of comparison with the above forms of albumose.

2.5 grams were ground fine with 50 cc. of water and then allowed to stand for several days without warming, a little thymol being added to prevent decomposition. Crystals of salt added to the clear acid filtrate produced a heavy precipitate, also when added to the neutralised or faintly alkaline (with sodium carbonate) solution. In a solution made quite strongly alkaline, however, the salt produced more of a turbidity than a compact flocculent precipitate. The entire solution of the substance precipitated with salt and filtered was not at all affected by dilution with a large quantity of saturated salt solution. With nitric and acetic acid, however, the solution was rendered somewhat turbid; excess of acetic acid rendered the solution clear again. The precipitates formed by these two acids were quite small, especially in comparison with the first precipitate produced by salt alone. The salt precipitate, pressed on the filter, dissolved in water and separated a second time by trituration with an excess of sodium chloride, again yielded a filtrate, precipitable by both nitric and acetic acid. Thus the agreement with protalbumose is quite evident. Certain detection of deuteroalbumose, which was probably also present, had to be given up on account of the small amount of material.

[1] Zeitschrift für Biologie, **19**, 159, also **19**, 209.

As the preserved urine-albumose was in great part insoluble in water, and as this insoluble portion melted by boiling in exactly the same manner as hetero- and dysalbumose, becoming emulsionised and afterwards hardening to a leather-like mass, we thought it best to examine the residue remaining after thorough washing with cold water, for these two forms of albumose. This residue, as reported in the previous publication, gave up something to 5 per cent. sodium chloride, which showed the general reactions of hemialbumose. This we found to be the case also in the present instance. The amount of substance dissolved, however, was too small, even from 5 grams of fresh material, to identify it with certainty as heteroalbumose, which can be conveniently done only through its separation by long-continued dialysis.

The residue remaining after treatment with salt solution was scarcely at all diminished in bulk, and was more than sufficient to furnish proof that it consisted of dysalbumose. This was plainly demonstrated by the fact that after complete extraction with water the residue dissolved almost completely both in 0.2 per cent. hydrochloric acid and in 2.5 per cent. sodium carbonate in ½–1 hour *without warming*. On neutralisation the substance was only partially precipitated; a portion of the precipitate was soluble in 5 per cent. sodium chloride. That portion of the neutralisation precipitate insoluble in sodium chloride can be considered as unaltered dysalbumose, while the portion taken up by the salt solution was naturally to be considered as converted into heteroalbumose.

Contrary to all expectation, however, the salt solution did not act like a solution containing heteroalbumose; it was only rendered slightly turbid by crystals of salt, while the filtrate gave an abundant precipitate on the addition of acetic acid containing salt. Heteroalbumose obtained by digestion, on the contrary, is readily precipitated by solid salt, and although never completely, it separates to such an extent that the addition of acetic acid afterwards produces only a strong opalescence. The principal difference, however, consisted in the fact that the united solutions after two days dialysis, at which time every trace of chlorine had disappeared, showed hardly any trace of turbidity, and nothing had apparently been deposited on the walls of the parchment tubes. In this purified condition the clear filtered solution of slight alkaline reaction gave a heavy coagulum by warming, without becoming in the least transparent on boiling. The solution was likewise precipitated in

the cold by nitric acid, which even in great excess did not produce a complete clearing of the solution, but left a large residue of yellow flocks.

Possible contamination with ordinary albumin might seem at first as the probable explanation of this appearance, but this was shown not to be the case by the ordinary hemialbumose reaction, since the substance precipitated in the cold by nitric acid dissolved on warming even in the slightest excess of acid and re-appeared on cooling.

The present investigation was begun in the hope of finding a satisfactory explanation for the very changeable behavior of the solutions and precipitate obtained in the primary digestive or other albuminous cleavage processes. It is our intention to continue our work in this direction. The first steps would appear now to have been accomplished since we have succeeded: 1st, in proving the existence of a row of bodies between albumins and peptones, the composition of which points to a gradual course of hydrolytic decomposition, and thus these forms of albumose are to be considered collectively as the first hydrates; 2d, in obtaining proof that the different forms of albumose not only fall apart into the anti- and hemi-group, but that now the hemi-group by itself can be considered as consisting of several members. According to all appearances also, this holds good not only for the cleavage products of fibrin, but also for those of albumin, myosin, etc., since we have frequently obtained after the digestion of such material, by the methods described in this paper, many products which at least are very similar to those described here.

Moreover, we are now in a position to explain the earlier found fact concerning "soluble" and "insoluble" albumose, as well as the contradiction regarding the precipitability of albumose, in part by sodium chloride alone and in part only by the united action of an acid.

What was previously designated "insoluble" hemialbumose consists of heteroalbumose, soluble only in boiling dilute sodium chloride, and which after once being boiled separates out in great part on cooling. "Soluble" hemialbumose corresponds to both protalbumose and deuteroalbumose, or to a mixture of both of these bodies. When protalbumose is obtained free from deutero-albumose, it is at once evident, from the fact that the latter cannot

be precipitated by sodium chloride alone; but since we have become familiar with heteroalbumose, it is also clear that in the majority of cases the precipitate obtained by simple addition of sodium chloride cannot be pure protalbumose, as there remains mixed with it a portion of heteroalbumose which can be separated by dialysis. On the other hand, it is less clear how a complete separation of deuteroalbumose from protalbumose is accomplished; for while it is a very easy matter to obtain the latter free from the first, the reverse, it would appear, must be correspondingly difficult, because the purified protalbumose is never completely separated by simple addition of salt, but is largely precipitated together with deuteroalbumose by the subsequent addition of acid. It would thus appear that deuteroalbumose can only be obtained contaminated with protalbumose. Yet, the above-described method of treatment of the commercial albumose mixture has furnished us the body so pure that its neutral solution was not made at all turbid by solid sodium chloride, a pleasant circumstance, which afterwards astonished us the more when we found that with our present means it is impossible to obtain the body pure again when it is mixed with ever so pure a solution of protalbumose. Probably the peculiar intermingling of protalbumose with hetero- and dysalbumose as found in Witte's preparation, is the reason of the complete insolubility of the former when the powder is at first treated with solid sodium chloride and salt solution, so that then deuteroalbumose goes into solution at the outset quite free from its obstinate companion.

The earlier statements regarding the turbidity and precipitation of hemialbumose by neutralisation, as also its precipitation, after the manner of albuminates, from solutions originally non-precipitable after their solutions have been treated with caustic alkalies or strong acids, find their explanation in the properties of hetero- and dysalbumose already described. It is hardly necessary to mention that such appearances can be observed in the case of prot- and deuteroalbumose, only when extraordinarily concentrated solutions or solutions rich in salt are used.

A comparison of the analytical results obtained from the separate forms of albumose with those obtained earlier,[1] shows the closest agreement in the majority of cases; thus, "soluble hemialbumose *B*" from fibrin was composed of C 50.40, H 6.69, and

[1] Compare Zeitschrift für Biologie, **19**, 193.

N 17.37 per cent. On the other hand, a very noticeable difference is found in the composition of the albumose from urine, which contained C 52.13, H 6.83, and N 16.55 per cent., and thus agrees the least in composition with the remaining samples of hemi-albumose obtained from the earlier preparations from both albumin and fibrin. We surmise that the reason of this, as well as of the other difference noticed in testing for heteroalbumose, is to be found in the origin of the urine albumose. The nature of the albuminous matter from which it originated is too little known, and on the same grounds we consider it very desirable that the forms of albumose of all of the albuminous bodies, viz. of serum-albumin, globulin, myosin, etc., should be investigated in the same manner as those of fibrin.

That we have in the present article explained all and each of the remarkable reactions which are to be observed in the digestive mixtures of albuminous matter we do not once imagine; thus, we still remain in doubt as to the reason of the paradoxical appearance recently noticed in the digestive mixture containing albumose (freed from neutralisation precipitate), where the solution containing a certain amount of salt is plainly coagulated by boiling only to become clear again on cooling; a most complete reversal of the most general of all albumose reactions.

We deemed it of considerable interest to see whether there were among the new-found bodies any which did not belong to the hemi-group. In our search after a pure hemialbumose which should be *completely* decomposed by trypsin, that is to say converted into amido-acids, etc., without a trace of peptone or albuminous body remaining, we have perhaps pursued a phantom. The experiment, however, was needed to discover whether or not there was concealed in the hemialbumose a residue of the anti-group. To this question a positive answer was at once obtained, for it was found that both hetero- and dysalbumose do not belong exclusively to the hemi-group. Originally of the opinion that these bodies would fill up the gap in the scheme of albumin cleavage previously devised by one of us, and that a hemialbumat would be revealed, we must now, after the results of the analyses which have given much too low percentages of carbon for the conjectured anhydride, turn our attention to some other view.

Of all the primary cleavage products, antialbumose is, up to the present, the most difficult to obtain, and at the same time is the

least known. That this product is represented by a single body is, after the new experiences with hemialbumose, hardly to be supposed, and thus the possibility is suggested that a portion of the constituents of which hemialbumose is now known to be composed, constitute in part antialbumose. Trypsin digestion was employed as a means of determining this point. The digestion was made first of all with prot- and deuteroalbumose, partially in aqueous solution and in part with the addition of one per cent. sodium carbonate, and certainly so large an amount of leucin, tyrosin, as well as the body colored violet by bromine, together with so small an amount of peptone, was never obtained from any of the earlier preparations of hemialbumose. These experiments, on account of the difficulty of preparing peptone-free trypsin, are not yet completely finished, and not yet decisive as to the complete removal of all matter of the anti-group from these two bodies. On the other hand, we can say with certainty from the first experiments with heteroalbumose, that this substance contains bodies of the anti-group, for we obtained from it by the action of trypsin non-decomposable *antialbumat*, changeable only into peptone.

Four grams of colorless glassy heteroalbumose, coming from a fibrin-pepsin digestion and twice purified, were dissolved in 200 cc. of 0.5 per cent. sodium carbonate, and warmed at 40° C. with about 1 gram of purified trypsin. The trypsin was not entirely free from peptone, but contained no trace of leucin, tyrosin, or other crystalline body, and a concentrated solution gave no color whatever with bromine water. After two hours the clear digestive mixture began to grow turbid, and at the end of six hours this turbidity had increased to a semi-gelatinous coagulation, which had all the appearances of the albumid coagulum. After filtration from this precipitate the fluid did not become turbid again by further warming at 40° C., neither was it rendered turbid by neutralisation nor by slightly acidifying. Evaporated and then extracted with alcohol it gave the usual peptone precipitate, coming in part without doubt from the trypsin, together with a crystalline deposit of leucin and tyrosin; moreover, a much more intense violet bromine reaction was obtained than would ordinarily be expected from the small amount of amido acids present. Bodies of the hemi-group are therefore contained in the heteroalbumose, and since it is evident both from the composition and reactions of the latter that undecomposed

albumin cannot be the cause of its peculiarities, it must therefore be a mixture, probably of hemi- and antiheteroalbumose.

The coagulum produced by trypsin was easily proved to be antialbumat, for on being dissolved in 0.2 per cent hydrochloric acid and mixed with very active purified gastric juice which gave no precipitate itself on neutralisation, and kept at 40° C. for 48 hours, it separated out on neutralisation apparently not at all diminished in amount; it was thus non-digestible in gastric juice. Warmed again with sodium carbonate, this time in a 1 per cent. solution, and then mixed with trypsin, the body separated from the solution a second time, although in smaller quantity than at first; and finally after 5 days continued digestion, with gradual addition of sodium carbonate until the mixture contained fully 3 per cent. of alkali, we succeeded in bringing it wholly into solution with the exception of a slight turbidity. After filtration through paper the fluid then remained unaltered during 8 days longer digestion. Neutralised with acetic acid the fluid gave no precipitate whatever, and in spite of the most careful and repeated treatment with alcohol nothing was found in the fluid other than peptone (antipeptone); not even a trace of leucin or tyrosin was to be detected, and with bromine water no indications of a violet or rose color. Thus the product separated as a coagulum by trypsin was found to be soluble and digestible in the presence of a sufficient amount of alkali, but like bodies of the anti-group was only convertible into peptone, not decomposable by the digestive mixture.

At the conclusion of this experiment another test was tried directly with heteroalbumose obtained from Witte's preparation; that is to say, the preparation without previous conversion into the albumat was treated with gastric juice, in order to see whether the supposed antiheteroalbumose is so difficultly or so slowly digestible in pepsin as is known to be the case with antialbumose in general. 4 grams of the substance were dissolved in 200 cc. 0.2 per cent. hydrochloric acid, and then mixed with an equal quantity of pure dialysed gastric juice of the same degree of acidity. A small portion of the mixture dissolved a piece of fibrin completely in five minutes, the fluid was therefore active. After eighteen hours warming at 40° C. it appeared, judging from the heavy neutralisation precipitate obtained in a portion tested, hardly at all digested, and not until the mixture had been warmed for five days was the heavy flocculent neutralisation precipitate obtained in a portion with-

drawn from the mixture, replaced by a turbidity. But even then when the entire quantity was neutralised an almost resinous precipitate was obtained, while in the filtrate a heavy turbidity was produced by sodium chloride and nitric acid, which disappeared on the application of heat, reappearing again as the solution cooled; a reaction naturally to be referred to the incomplete precipitation of heteroalbumose by neutralisation.

We cannot but think that dysalbumose, coming as it does from heteroalbumose, will show a similar behavior towards pepsin and trypsin digestion, and we hope in the near future to demonstrate this, as well as several other suppositions, by a continuation of our present line of work.

Addenda.

In order to obtain further knowledge of the rotary power of these forms of albumose, we have, since the above was written, made in addition to the observations in dilute acid solutions already described, several experiments, both in faintly alkaline solutions and in sodium chloride solutions, with the following results:

Protalbumose A.

1.1088 grams previously dried at 105° C. = 1.0989 grams ash-free substance dissolved in 40 cc. H_2O + 10 cc. 0.6 per cent. Na_2CO_3 = 0.021978 gram substance per cubic centimetre, gave with the fluid at 20° C.:

In 200 mm. tube as a mean of 4 observations — 3.55° rotation, therefore $(a)_D = -80.76°$;

In 220 mm. tube as a mean of 4 observations — 3.95°, therefore $(a)_D = -81.69°$.

Protalbumose B.

1.1362 grams = 1.1337 grams ash-free substance in 41 cc. H_2O + 10 cc. 0.6 per cent. Na_2CO_3 = 0.022229 gram per cubic centimetre, gave at 21° C.:

In 200 mm. tube as a mean of 5 observations — 3.12°, therefore $(a)_D = -70.17°$;

In 220 mm. tube as a mean of 7 observations — 3.54°, therefore $(a)_D = -70.93°$.

Protalbumose C.

I. 0.9610 gram = 0.9363 gram ash-free substance in 40 cc. H_2O + 10 cc. 0.6 per cent. Na_2CO_3 = 0.018726 gram per cubic centimetre, gave with the solution at 23.5° C.:

In 200 mm. tube as a mean of 7 observations — 3.0°, therefore $(a)_D = -80.10°$;

In 220 mm. tube as a mean of 8 observations — 3.3°, therefore $(a)_D = -80.10°$.

II. 1.2115 grams = 1.1803 grams ash-free substance in 40 cc. H_2O + 10 cc. 0.6 per cent. Na_2CO_3 = 0.023606 gram per cubic centimetre, gave at 22.5° C.:

In 200 mm. tube as a mean of 5 observations — 3.74°, therefore $(a)_D = -79.21°$;

In 220 mm. tube as a mean of 8 observations — 4.11°, therefore $(a)_D = -79.14°$.

Protalbumose D.

0.7490 gram = 0.7411 gram ash-free substance in 40 cc. H_2O + 10 cc. 0.6 per cent. Na_2CO_3 = 0.014822 gram per cubic centimetre, gave with the solution at 21° C.:

In a 200 mm. tube as a mean of 7 observations, a rotation of — 2.1°, therefore $(a)_D = -70.84°$.

Protalbumose E.

I. 0.9645 gram = 0.9518 gram ash-free substance in 40 cc. H_2O + 10 cc. 0.6 per cent. Na_2CO_3 = 0.019036 gram per cubic centimetre, rotated the light with the temperature of the fluid 24.5° C.:

In 200 mm. tube as a mean of 6 observations — 2.90°, therefore $(a)_D = -76.17°$;

In 220 mm. tube as a mean of 6 observations — 3.20°, therefore $(a)_D = -76.41°$.

II. 1.2637 grams = 1.2471 grams ash-free substance in 40 cc. H_2O + 10 cc. 0.6 per cent. Na_2CO_3 = 0.024942 gram per cubic centimetre, rotated the light with the fluid at 24.5° C.:

In 200 mm. tube as a mean of 8 observations — 3.79°, therefore $(a)_D = -75.97°$;

In 220 mm. tube as a mean of 8 observations — 4.10°, therefore $(a)_D = -74.72°$.

Deuteroalbumose F.

I. 1.4205 grams = 1.3954 grams ash-free substance in 45 cc. H_2O + 10 cc. 0.6 per cent. Na_2CO_3 = 0.0253709 gram per cubic centimetre, rotated the light with the solution at 23° C.:

In 200 mm. tube as a mean of 8 observations — 3.77°, therefore $(\alpha)_D = -74.29°$;

In 220 mm. tube as a mean of 8 observations — 4.33°, therefore $(\alpha)_D = -77.57°$.

II. 0.6549 gram = 0.6434 gram ash-free substance dissolved in 50 cc. 0.5 per cent. NaCl = 0.012868 gram per cubic centimetre, rotated the light with the solution at 22° C.:

In 200 mm. tube as a mean of 5 observations — 2.0°, therefore $(\alpha)_D = -77.71°$;

In 220 mm. tube as a mean of 6 observations — 2.18°, therefore $(\alpha)_D = -77.00°$.

Deuteroalbumose G.

I. 0.9065 gram = 0.9004 gram ash-free substance in 41 cc. H_2O + 10 cc. 0.6 per cent. Na_2CO_3 = 0.0176549 gram per cubic centimetre, rotated the light, the solution at a temperature of 22.5° C.:

In 200 mm. tube as a mean of 6 observations — 2.68°, therefore $(\alpha)_D = -75.90°$;

In 220 mm. tube as a mean of 6 observations — 2.90°, therefore $(\alpha)_D = -74.66°$.

II. 1.0419 grams = 1.0349 grams ash-free substance in 54 cc. 0.5 per cent. NaCl = 0.0191648 gram per cubic centimetre, rotated the light with the solution at 22° C.:

In 200 mm. tube as a mean of 7 observations — 2.73°, therefore $(\alpha)_D = -71.22°$;

In 220 mm. tube as a mean of 7 observations — 3.07°, therefore $(\alpha)_D = -72.81°$.

Heteroalbumose H.

0.8154 gram = 0.8081 gram ash-free substance was dissolved in 36 cc. H_2O + 10 cc. 0.6 per cent. Na_2CO_3 + 5 cc. 2 per cent. Na_2CO_3 (a clear solution was not obtained until the addition of the stronger solution of alkali) = 0.015845 gram per cubic centimetre. On account of the opalescence of the solution it was examined only in a 100 mm. tube, and with the solution at 20° C. it rotated the light as a mean of 7 observations — 0.96°, therefore $(\alpha_D) = -60.58°$.

The average results obtained in both acid and alkaline solutions are represented for the sake of comparison in the following table:

	Protalbumose.			Protalbumose.		Deuteroalbumose.		Heteroalbumose.	
	A.	B.	C.	NaCl Precip. D.	Acid Precip. E.	F.	G.		
Acid solution.....	−72.64°	−79.05°	−77.90°	−73.18°	−71.40°	−74.41°	−79.11°	−68.65°	$(a)_D$
Alkaline solution..	−81.22°	−70.55°	−79.64°	−70.84°	−75.82°	−75.93°	−75.28°	−60.65°	
NaCl solution.....	..	..	..	..	..	−75.35°	−71.96°	..	

REVIEWS AND REPORTS.

The Artificial Preparation of Optically Active Substances.

Chemists generally assume that all chemical substances can be made in the laboratory by artificial methods, and certainly when we consider the many syntheses of natural substances that have been effected during the last thirty years, the assumption appears to be justified. Nevertheless, there are some facts which speak against it. Several of the vegetable acids have the power of turning the plane of polarised light either to the right or left. Some of these substances have been prepared artificially, and the products thus obtained have been shown to have all the properties of the corresponding natural substances with the exception of the optical activity. Thus natural malic acid is laevo-rotatory, while the malic acid obtained from brom-succinic acid is optically inactive. Such facts have led gradually to the conclusion that artificially prepared substances cannot act upon polarised light, that in order to get an optically active substance we must have the intervention of the life process.

Finally, however, Perkin and Duppa succeeded in making racemic acid from bibrom-succinic acid, and Jungfleisch and Pasteur showed that this artificially prepared racemic acid could be split up into dextro- and laevo-tartaric acids. Thus the artificial preparation of one optically active substance was certainly accomplished, and, while some chemists concluded that the same result would probably in time be reached in connection with all optically active substances, others preferred to suspend judgment and await further developments.

Last December, M. Pasteur, in a lecture[1] before the Paris Chemical Society, called special attention to the subject. The lecture has given rise to an interesting discussion between MM. Wyrouboff, Jungfleisch and Pasteur, the substance of which, together with two papers on the subject by M. Jungfleisch, are published in the Bulletin de la Société Chimique de Paris, Vol. 41, No. 5 (March 5, 1884). In view of the interest which the subject must have for all chemists, abstracts of M. Pasteur's lecture and the other papers referred to are here given. M. Pasteur began his lecture by describing in detail the crystallisation of the double racemate of ammonium and sodium, and the formation of the two kinds of crystals from it. To use his own words: "A new idea soon occurred to me. These crystals, asymmetric to the right, which I could separate mechanically from the others, proved to be identical in form with those of the dextro-tartrate. . . I separated these right-handed crystals from the crystallised racemate; I made the lead salt and isolated the acid. This acid was absolutely identical with the tartaric acid from grapes, and, like it, acted upon polarised light. I was still happier when, on taking in turn the left-handed crystals obtained from the racemate, I obtained a tartaric acid quite similar to ordinary tartaric acid, but having a form asymmetrical in the opposite way, and acting in the opposite direction upon polarised light. The form was identical with that of the image of dextro-tartaric acid placed before a mirror. The principles of '*molecular asymmetry*' were thus founded. There are substances of which the atomic grouping is asymmetrical, and this grouping shows itself in an asymmetric form and in an action upon polarised light; besides, these atomic groupings have their possible complements, the forms of which are identical with the images of the first, and with an opposite action upon polarised light. . . .

"Now, gentlemen, there is one strange peculiarity about this molecular asymmetry. We find asymmetry established in a very large number of the proximate principles of animals and vegetables, notably in the proximate principles essential to life. All the products, so to speak, of the egg and the seed are asymmetrical.

"There are, without doubt, in animals and vegetables proximate principles, such as urea and oxalic acid, which are not asymmetrical; but these are secondary products, comparable in one sense to our laboratory products, which are not asymmetrical.

"In other words, when a ray of sunlight strikes a green leaf, when the carbon of carbonic acid, the hydrogen of water, the nitrogen of ammonia, and the oxygen of the carbonic acid and of the water form chemical compounds, and the plant grows, the bodies which are thus developed are asymmetrical. You, however, skillful chemists as you are, though you bring together the same elements in a thousand different ways, always make products without

[1] Revue Scientifique, Jan. 5, 1884.

molecular asymmetry. As far as I know, there does not exist a single product of chemical synthesis, formed under the influence of causes which may be considered peculiar to vegetable life, which is not asymmetrical. . . On the other hand, there is not a single product of synthesis prepared in the laboratory or in dead mineral nature, which is not symmetrical."

The speaker then referred to the synthesis of racemic acid from bibrom-succinic acid, and the splitting up of this artificial product into dextro- and laevo-rotatory tartaric acids. He denied that this synthesis disproved his statement that optically active substances cannot be prepared synthetically. He quoted the words of Le Bel, as follows: "It is then not only vegetable life which includes cases of asymmetry, and the line of demarcation between vegetable and mineral chemistry pointed out by M. Pasteur does not exist." To this he remarked: "That is an error. I claim to be able to show you that this separation, this barrier, is on the contrary confirmed by the results first observed by myself, and afterwards by M. Jungfleisch and by M. Le Bel.

"We can explain the facts regarding asymmetry in the following manner: When the proximate principles which are essential to life are formed, it is under the influence of asymmetrical forces, and that is why life produces asymmetrical substances. When the chemist in his laboratory combines the elements or compounds formed from the elements, he does not bring into play the asymmetrical forces. That is why all the substances which he produces by synthesis are devoid of asymmetry. . . . You ask: what then are the asymmetrical forces which preside over the elaboration of the proximate principles of nature? It would be difficult for me to answer with accuracy; but asymmetry I see everywhere in the universe. The universe is asymmetrical. . . . You in your laboratories, with your solvents, your heat and cold, have at your service only symmetrical forces. Is there then an absolute division? Certainly not. Far from saying or thinking so, I first pointed out the means which we might make use of to destroy the barrier. What must we do to imitate nature? We must break loose from our methods, which are from this point of view antiquated and impotent. We must try to bring into action the asymmetrical forces, we must have recourse to the action of the solenoid, of magnetism, of the asymmetrical motion of light, to the action of substances which are themselves asymmetrical. When, carried away by inexorable logic, I passed from researches in crystallography and molecular chemistry to the study of ferments, my thought was to introduce asymmetry into chemical phenomena. . . . On bringing together cinchonine, an active asymmetrical substance, and racemic acid, I saw the cinchonine salt of laevo-tartaric acid deposited, while the dextro-tartrate remained in solution. With an inactive body, racemic acid, I have made laevo- and dextro-tartaric acids. Although I was the first to imitate nature in its methods, and to show the analogy between natural

and artificial products, I am careful not to conclude that the barrier between the two chemistries is destroyed. On the contrary, I conclude that the experiment of which I have spoken establishes the proposition, namely, that the forces brought into play in our laboratories differ from those to which vegetable nature is subject.

"In another way, much more interesting, I have introduced asymmetry into chemical actions. I have shown that ammonium racemate can ferment under the influence of microscopic fungi, and that laevo-tartaric acid appears. The dextro-tartrate is decomposed, the laevo-tartrate remains intact. With an inactive racemate I have caused the appearance of simple asymmetry, but why? Because the little ferment is a living body formed of a collection of asymmetrical products, and because for purposes of nutrition the little being finds the dextro-tartrate better adapted than the laevo-tartrate.

"I have gone further: I have caused to grow on the surface of ashes and racemic acid, some grains of *Penicillium glaucum*, that mould which is found everywhere, and I have seen laevo-tartaric acid appear. Here again we have a case of simple asymmetry obtained from an inactive body; but in order to reach this result, it has been necessary, you see, to cause the intervention of the actions of asymmetry, the asymmetry of the natural proximate principles which go to make up the grain of mould.

"These are precisely the methods made use of by M. Le Bel in extracting from his racemates the simple active products. He had recourse to the employment of an asymmetrical substance or of a mould or a microbe.

"Further, these experiments indicate the existence of a line of demarcation between the mineral kingdom and the organic kingdom, since to imitate what nature does, that is to prepare a right-handed or a left-handed body, we are obliged to make use of peculiar kinds of action, of the action of asymmetry. The line of demarcation of which we speak is not a question of pure chemistry, of obtaining such and such products, it is a question of forces; life is governed by asymmetrical actions." . . . In a note M. Pasteur adds these words: "I am convinced that the double racemate of sodium and ammonium would not of itself under ordinary circumstances break up during crystallisation unless an asymmetric force were present, and if this is not an action of light or magnetism, I can readily believe that the force is due to some asymmetrical organic dust on the surface of the vessel in which the crystallisation takes place. Nothing would be simpler than to crystallise a solution of sodium-ammonium racemate with perfect exclusion of all organic dust. Under such circumstances the unchanged racemate should be obtained."

Discussion.

M. Wyrouboff said that the theories put forward by M. Pasteur with so much conviction and talent, in his lecture, appeared to him

to be opposed to all that is known to us regarding the properties of crystallised bodies. The theories are based upon a fundamental hypothesis, according to which natural (chemical) phenomena are subject to two kinds of action: symmetrical and asymmetrical; the former governing in the mineral kingdom and in the syntheses effected in our laboratories, the latter pertaining to the life process.

Asymmetrical bodies may be arranged, as is known, in two well characterised classes. Those of the first class, like quartz, sodium chlorate, benzil, cinnabar, are asymmetrical either in their internal structure and their external form, or only in their internal structure, no hemihedral face accompanying the rotatory power. All these bodies can be prepared artificially by starting with the elements; hence we must admit, looking at the matter from M. Pasteur's standpoint, that in our laboratories we have at our disposal at least some of the asymmetrical actions which he attributes exclusively to life; for, how shall we explain, by the aid of symmetrical actions alone, the existence of plagihedral faces of crystals and their relation to the rotatory power?

"The second category includes those bodies which are not asymmetrical in their internal structure, but have asymmetrical external forms and integrant molecules, or only the latter, for, between the rotatory power of the solution and the hemihedrism of the crystals, there is not that simple and necessary relation which was supposed to exist when only a few facts were known. These bodies have the rotatory power only in solution, and retain the power in all the compounds into which they enter. They are asymmetrical neither more nor less than the bodies of the first category; they are asymmetrical in a different sense.

"The bodies which have molecular asymmetry are the ones which M. Pasteur had in view when he asserted that they cannot be prepared synthetically.

"It should be remarked in the first place, that, among the great number of compounds which chemists have prepared synthetically, only very few have been studied crystallographically and examined with the polariscope. In the second place, the assertion is contradicted by the facts: racemic acid has been prepared synthetically, and it has been split up into dextro-rotatory and laevo-rotatory tartaric acids. To this proof, so clear and definite, M. Pasteur replies by suggesting a new hypothesis. He asserts that we really have to deal with some action of the asymmetrical order, some spiral movement, some magnetic influence, some organic dust, and he adds: 'Nothing would be simpler than to crystallise a solution of sodium-ammonium racemate with perfect exclusion of all organic dust. Under such circumstances the unchanged racemate should be obtained.' But what is the object of trying this experiment, when we consider that twenty years ago the racemate of the formula $C_4H_4Na(NH_4)O_6 + H_2O$ was prepared by M. Scacchi, who, in an admirable memoir, gave the exact conditions of its formation? He showed that the splitting of the acid was occasioned

only by the fact that the double ammonium sodium salts of the two tartaric acids are less soluble than the mixture of the two; that in elevating the temperature, the solubility of the dextro-acid increases more rapidly than that of the laevo-acid, and that there is a limit beyond which the mixture, becoming less soluble, the racemate alone is deposited. The phenomenon is so perfect that we can get at will from the same solution, properly concentrated and containing an excess of ammonium carbonate, either the racemate, or ammoniacal Seignette salt, or crystals of both at the same time. It is only necessary to vary the temperature between 17° and 26°. The racemate of sodium and potassium conducts itself differently: at 26° it always splits up; below this temperature it deposits sodium racemate, then Seignette salt, finally sodium racemate, each one of the deposits corresponding to the solubility of the salt, as M. Scacchi has shown.

"With sodium-thallium racemate the case is still different. M. Wyrouboff has recently prepared this salt, and will soon describe its form. Seignette salt containing thallium crystallises, as is known, between 20° and 25° in voluminous soluble crystals in about half their weight of water. Neutral thallium racemate requires at these temperatures about nine parts of water to dissolve it; neutral sodium racemate about 2.5 parts.

"According to M. Pasteur, it would be impossible to say beforehand whether or not the racemate will be split into the dextro- and laevo-tartrates, the splitting being a result of mysterious forces acting asymmetrically.

"Nothing is easier, however, than to foresee the course of the phenomenon, if it really depends upon the greater or less solubility of the compounds taking part in the crystallisation. On evaporating at 25° we ought not to get the double tartrate; nor even the double racemate, unless it is—what it is not—less soluble than the neutral tartrate of thallium; we could get only thallium racemate; later, after the liquid is further concentrated, a little of the double racemate, and lastly, sodium racemate. This indeed is what is always observed. And it is so clearly a matter of solubility, that we may get the double racemate of sodium and thallium by two methods, apparently different, but based upon the same principle: we can crystallise the mixture at an elevated temperature, 40° for instance, or at the ordinary temperature, adding an excess of sodium racemate.

"Finally, we have the double racemate of sodium and rubidium, which under the proper conditions always breaks up at ordinary temperatures, and the two simple salts separate at higher temperatures.

"These examples enable us to solve without difficulty the general question as to the causes of the splitting of the racemates, which appears so complex and so mysterious to M. Pasteur, and which is nevertheless so simple. Why do not all the numerous racemates, simple as well as double, known up to the present time,

yield tartrates? Why is this action confined to the double salts of sodium, with potassium, ammonium and rubidium? Because, in these cases alone, one of the tartrates taken separately is less soluble at the ordinary temperature than the mixture of the two.

"We may hence state these rules, to which up to the present there are no exceptions known:

1. *Every racemate having a solubility less than that of the corresponding tartrate splits up;*

2. *Every racemate which is more soluble than the corresponding tartrate does not split up.*

Finally, concerning the case of double racemates,—and this applies to double salts of all possible acids:

3. *When two simple racemates, which are allowed to crystallise together, have very different solubilities, they are deposited separately. To get the double salt, the proportion of the more soluble salt must be increased.*

"The solubility being a function of the temperature, it is clear that these rules are valid for any given compound only at a definite temperature."

A propos of the communication of M. Wyrouboff, M. Jungfleisch cited a number of facts which have led him to the opinion that the separation or non-separation of inactive bodies into their constituents is a result of the relations which exist between the solubilities. Thus, in a solution of sodium ammonium racemate, the dextro-tartrate resulting from the splitting up shows itself to be less soluble than the laevo-tartrate. Some experiments have indicated that differences of the same kind exist between the two active tartrates of sodium and potassium. Besides, it is known that the corresponding racemate obtained by M. Delffs was deposited in the neighborhood of 0°. Further, we may recall the tartrates of cinchonine of M. Pasteur: the marked differences which exist between their solubilities suffice to explain their separation. Finally, the phenomena observed by M. Jungfleisch on para-camphoric acid furnishes new insight from this point of view: during the cooling of a warm solution of this body between 80° and 40°, principally the laevo-acid is deposited, while the dextro-acid predominates in the crystals formed below 40°; the solubility curves are so different that the two optically active acids can be separated by fractional crystallisation. If the mother-liquor is allowed to stand in the cold, para-camphoric acid is again formed.

M. Pasteur's Reply to M. Wyrouboff.

"I am very much surprised that M. Wyrouboff should have confused molecular asymmetry and the asymmetry in the arrangement in a crystal. Is not the difference between the two kinds of asymmetry demonstrated by the fact that fused quartz dissolved, sodium chlorate dissolved, strontium formate dissolved, have no action on polarised light; that, on the other hand, an asymmetrical

crystal, right or left handed, of one of these substances, as sodium chlorate for example, gives, when crystallised, two sorts of hemihedral crystals?

"M. Wyrouboff objects to the hypothesis which I suggested in a note concerning my communication to the Chemical Society on the 22d of December, which was to the effect that the splitting of sodium ammonium racemate may be caused by organisms in the solution or on the crystallising dishes. As far as I am concerned, that is merely a preconceived notion, but I give it for what it is worth. *A priori* ideas, hypotheses, with all due deference to my opponent, are essential to scientific progress.

"If the experiment which I have referred to should not prevent the splitting of the racemate, I shall try whether the splitting may not be due to some other cause equally asymmetric, for example, light, or terrestrial magnetism.

"M. Wyrouboff seems to think the matter is settled when he assures us that the conditions of the formation of the racemate and of the splitting of the racemate are now well known, and that they depend upon the greater or less solubility of the salts. But M. Wyrouboff, in my opinion, seems not to comprehend the fact that the formation of the racemate is only perfectly natural, as all the racemates, with one exception, occur only as such; what is exceptional is that one racemate should split up. I cannot consider the opinion reasonable that finds the cause of the splitting in an influence of solubility. Why does the racemate of sodium and ammonium deposit crystals of two kinds, why does it give rise to the formation of complementary tetrahedrons? Why do these two tetrahedrons exist, and why not the octahedron which corresponds to them, which octahedron would have the solubility of the tetrahedral crystals? These facts, according to my idea, require explanation. I shall continue to believe, as long as I am not shown to be wrong, that the splitting can take place under the influence of asymmetry.

"M. Wyrouboff, in another part of his remarks, calls my attention to the existence of bodies which are active towards polarised light, but which nevertheless have no asymmetry of form. He who reproaches me for not understanding the subject, appears not to be aware that I have formerly examined into this fact with much care, and that I have shown that it is easy, by means of artifices in crystallisation, to cause the appearance of asymmetric faces whenever internal molecular asymmetry exists. I cited the case of tartramide, the crystals of which formed in pure water never have hemihedral faces, but which show these faces when they are deposited from an ammoniacal solution. I cited the case of ammonium bimalate, which in crystallising from pure water never has hemihedral faces, and which has them when the liquid in which the salt crystallises is changed by a very simple process to which I refer.

"M. Wyrouboff makes a great deal out of the following fact:

On adding ammonium citrate to ammonium (dextro) tartrate, the hemihedral faces appear on the other side of the crystal, and inversely for the laevo-tartrate, and, he adds, the hemihedrism may be made to disappear entirely. But this is only one of the accidents of crystallisation of which I have given many examples; I have proved that crystals of right-handed Seignette salt are sometimes met with which have left-handed hemihedral faces. A crystal may have a number of secondary forms. The hemihedral faces make a part of the secondary forms, and these show themselves or are absent according to the conditions of temperature, of the medium, etc., etc. One can not see why the external conditions of crystallisation should not overcome the influence of the asymmetric agency upon the internal structure of the molecules."

Experiments of M. Jungfleisch.

M. Jungfleisch describes some new experiments which tend to show that the dextro- and laevo-tartrates of sodium and ammonium have different solubilities in a solution of a mixture of the two salts. He introduced into a supersaturated solution of the racemate a right-handed crystal and a left-handed crystal. The two salts were deposited at once. The crystals were weighed in a number of cases and constant results were obtained. The following examples will indicate the character of these results:

I. Experiment with 1545 grams racemic acid:
Crystals of the first deposits: left, 557 gr.; right, 585 gr.
Crystals of the last deposits: left, 581 gr.; right, 569 gr.
II. Experiment with 1500 grams racemic acid:
Crystals of the first deposits: left, 561 gr.; right, 577 gr.
Crystals of the last deposits: left, 533 gr.; right, 488 gr.

In another case, starting with two kilograms of racemic acid, successive deposits were obtained as follows:

First crystallisation: laevo salt, 375 gr.; dextro salt, 400 gr.
Second crystallisation: laevo salt, 160 gr.; dextro salt, 181 gr.
Third crystallisation: laevo salt, 165 gr.; dextro salt, 190 gr.
Fourth crystallisation: laevo salt, 115 gr.; dextro salt, 115 gr.
Fifth crystallisation: laevo salt, 185 gr.; dextro salt, 150 gr.

In all the experiments the right-handed salt is at first deposited in greater quantity than the left-handed; its solubility is hence less than that of the left-handed salt. Inversely, in the second phase of the crystallisation the left-handed salt appears more abundantly than the right-handed.

Further, when a solution of sodium ammonium racemate is concentrated to such an extent that, on cooling, it deposits about half of the mixture of the two tartrates which it can yield, it is found that the mother-liquor has a rotatory power to the left, slight to be sure, but quite sufficient to be easily observed. Hence the left-handed salt exists in the mother-liquor in larger quantity than the right-handed salt; it is more soluble than the latter.

M. Jungfleisch finally states that the discussion between himself and M. Pasteur is based on a misunderstanding. M. Pasteur wishes to make a simple active body without passing through a body inactive by compensation, that is decomposable into right and left-handed substances; he wishes not simply to make racemic acid, which is decomposable into the two active tartaric acids, but to make directly a single one of the two latter. M. Pasteur wishes to follow the method of nature, which produces the dextro-acid and not racemic acid. This seems to M. Jungfleisch to be an entirely distinct problem, and it has not been solved up to the present, though the preparation of an optically active substance by methods independent of the life process has been accomplished. He is willing to go further and say that the problem of imitating the processes of nature has been solved neither for optically active nor for optically inactive substances. "The time when M. Berthelot established the possibility, till then denied, of producing synthetically the natural proximate principles is still not far removed, and although the results obtained in this way are as important as they are numerous, the state of science does not yet enable chemists to copy the actual *processes* of nature. Though M. Berthelot, M. Würtz, MM. Gräbe and Liebermann, or M. Baeyer, have effected the syntheses of alcohol, of the oil of mustard, of neurine, of alizarin and of indigo, they have not been able to copy the natural methods of formation of these substances, the natural methods remain unknown; they have, nevertheless, been of the opinion that a great step was taken in pointing out *any method whatever* by which these bodies can be produced without the intervention of the plants and animals." I. R.

THE UNION OF BODIES BY PRESSURE.

It has been known for some time that two pieces of ice, when pressed together, provided their temperature is near their fusing point, unite and form one homogeneous mass. Nor is this the only case of the kind known to us. Powdered sodium nitrate, perfectly dry and pure, when placed in a stoppered bottle and allowed to stand a long time, becomes a solid block. This block, it is true, can be broken very easily. But suppose the particles could by some means be brought more closely together, would it not follow that the union would be more perfect? And provided the particles could be brought within the range of molecular action, would not the result be the same as if there had been fusion of the mass? Gases are liquified by causing their molecules to come within the range of each other's action. From this it would seem naturally to follow that substances possessing an affinity for each other could be made to unite and form a *chemical compound* by the same process as that used in the liquefaction of gases.

Led by this kind of reasoning, W. Spring, in 1880, was induced to try the effect of pressure on a large number of bodies. He subjected various substances to great pressure, and announced the result of his experiments to the Royal Academy of Belgium.[1]

The apparatus used in effecting the pressure consisted of a stout lever moving on a horizontal axis. At the end of this lever heavy weights could be placed, and close to the axis there was a piston moving airtight in a steel cylinder. By the use of various weights at the extremity of the lever a pressure of 10,000 atmospheres was easily produced.

Filings of the various metals were placed in the cylinder and a pressure applied, increasing gradually until the desired effect was produced. In this way blocks of lead, bismuth, tin, zinc, aluminum, copper, antimony and platinum were obtained, that seemed to be homogeneous throughout. They had the specific gravity of ordinary fused metals; could be filed, sawed and hammered, and had all the other properties of homogeneous metals. Under the microscope there was no evidence of granular structure. This result, however, was not produced by one application of the pressure. The block obtained after the first application, was filed and the filings subjected again to increased pressure, until no evidence of pores could be detected under the microscope. Lead united under a pressure of 2000 atmospheres, bismuth at 6000, zinc at 5000 and copper at 6000. In no case was the temperature allowed to rise above 130°. At this temperature it was found that zinc united a little more readily than at a lower one. In all cases the block obtained was identical in appearance with that obtained by fusion. The bismuth, when struck, broke with a crystalline fracture, and possessed in common with the blocks of the other metals a highly metallic lustre. The ease with which the metals united seemed to be inversely proportional to their hardness.

A very interesting fact, noted in connection with lead especially, was its "flowing." In relation to this Spring says:[2] "Under a pressure of 5000 atmospheres, lead no longer resists the piston of the apparatus. It seemed *as if a liquid* were in all the cracks of the apparatus, and the piston was pressed to the bottom of the cylinder. When the apparatus was opened, thin coatings of the lead were found everywhere, which had the appearance of those obtained by plating."

When prismatic or amorphous sulphur was subjected to a pressure of 5000-6000 atmospheres, at the temperature 13°, an opaque block of rhombic sulphur was obtained, which was harder than that obtained by fusion. Its specific gravity was 2.0156, while that of the prismatic variety is 1.96. Its fusing point was 115°, that of ordinary rhombic sulphur being from 111° to 114°, and that of plastic sulphur 120°.

[1] Bulletin de l'Académie de Belgique, 2 serie, **45**, 746; **49**, 323. Ann. de Chim. et de Phys., 5 serie, **22**, 170.
[2] Bull. de l'Acad. Belg 2 ser. **49**, 323; Ann. de Chim. et de Phys. 5 ser. **22**, 170.

Amorphous phosphorus gave evidence of transformation into the crystalline variety.

Precipitated zinc sulphide under 5000 atmospheres gave a very hard, compact mass, whose exterior had a gray metallic lustre; the interior on the contrary appeared to be composed of a mass of crystal fragments, perfectly transparent, and reminded one of blende. The sulphides of lead and arsenic were obtained with the properties of the natural minerals to a greater or less extent. Carbon in the form of graphite united under a pressure of 5500 atmospheres, whereas that obtained by heating sugar gave not the slightest indication of union, but appeared to possess "great elasticity."

Copper filings and coarsely pulverised sulphur mixed together and subjected to 5000 atmospheres pressure, *combined chemically*, and formed a black crystalline mass of cuprous sulphide (chalcocite). An excess of sulphur had been used, and this excess could be detected with the microscope, disseminated through the mass of cuprous sulphide formed.

A coarse mixture of mercuric chloride and copper filings was put under 5000 atmospheres. There was complete change between the copper and the mercury. The copper had formed cuprous chloride with all the chlorine, and in place of the particles of copper little drops of mercury could be seen.

Dry potassium iodide and dry mercuric chloride, which gave no reaction under ordinary pressure, formed a red block of iodide of mercury and potassium chloride, when subjected to 2000 atmospheres.

In every case (except one[1]) tried with success, the product obtained had a smaller volume and a greater specific gravity than those of the substances used. Every attempt made to obtain a solid product of less specific gravity than the mean of the specific gravities of the substances used, failed. In general it appears that "the substance takes the condition corresponding to the volume to which the substances used are compressed."

In order to test further the correctness of this law, a mixture of bismuth, cadmium and tin, in proportions to form Wood's metal, was taken and subjected to 7500 atmospheres pressure at the ordinary temperature. A solid block was obtained. This was filed and resubjected to the same pressure. The alloy formed fused at 70°. Lead, bismuth and tin were taken in proportions to form Rose's metal. The resulting block melted in boiling water.[2]

Besides the substances mentioned, Spring claims to have succeeded in producing the sulphides[3] and arsenides[4] of many of the metals, and to have produced them with all the properties of the

[1] A mixture of sodium carbonate and arsenic pentoxide gave off carbon dioxide and formed sodium arsenate.

[2] Berichte der deutschen chemischen Gesellschaft, **15**, 595.

[3] Berichte der deutschen chemischen Gesellschaft, **15**, 999, and Bull. de l'Acad. de Belg. 3 ser. **5**, 492.

[4] Berichte, etc., **15**, 324; Bull. de l'Acad. de Belg. **5**, 229.

naturally occurring substances, especially as regards their crystalline structure.

Within the past year the accuracy of Spring's observations has been called into question by Friedel and Jannetaz of the French Chemical Society.

These gentlemen considered the question of so much importance as to warrant further study, and a repetition of Spring's experiments. Friedel[1] states that on subjecting various bodies to 10,000 atmospheres pressure he failed in every case to get complete union. Jannetaz,[2] working with Messrs. Neel and Clermont, subjected antimony, bismuth, tin, zinc, copper and iron to pressure, and obtained solid blocks, apparently homogeneous. The bismuth seemed to be more crystalline than the others, but was in reality only schistose in its structure. Bismuth, lead and tin in proportions to form Newton's metal, exhibited no indications of union.

Lead chloride formed a solid crystalline block, which probably owed its crystalline structure to the fact that the powder used was crystalline.

In compressing mercurous iodide a little escaped, and a small quantity of mercuric iodide was formed.

Powdered sulphur was mixed with zinc, iron, copper and lead filings respectively, in proportions to form blende, chalcocite, ferrous sulphide and galena. Pressure was applied, and the blocks formed were examined very carefully. They presented the general appearance of the substances to which their compositions corresponded. They were translucent at the edges and appeared to be crystalline. It was very difficult, however, to decide whether they were really crystalline or not, as under the microscope the crystalline powder used in the production of the blocks would interfere with the determination of the crystalline properties of the product.

On examination of their conduct toward heat, it was found that in the solid block, heat was propagated less easily in the direction of the pressure than perpendicularly to it. This has been shown to be a property peculiar to all bodies possessing a schistose structure. Now it is known that pressure produces this kind of structure, and Jannetaz claims that this is what has taken place in all the cases mentioned above. When the powdered blocks were treated with carbon bisulphide, the sulphur was dissolved and the particles of metal were left. In all cases, however, small quantities of the sulphides were formed, as was determined by grinding the product obtained with acid potassium sulphate, when a slight evolution of hydrogen sulphide was noticed. This is claimed as probably due to the heat produced by the pressure, and takes place more readily along the walls of the cylinder than in the interior of the mass. An incident is mentioned in this connection which shows that perhaps the heat produced by these enormous pressures is much greater than is generally supposed.

[1] Bull. de la Société chimique de Paris, **39**, 626. [2] *Ibid.* **40**, 51.

On subjecting a piece of bell-metal to a pressure of some seven or eight thousand atmospheres, the block burst and pieces flew past the operators and fell some distance off. On picking them up they were found to be covered with a coating similar to that found on meteorites. This may have been due, however, to the "flowing" noted in connection with Spring's experiments.

Up to the present time Spring has not replied to the statements of Friedel and Jannetaz, so that it is impossible to decide positively as to the value of his results. Before attempting to explain or make use of them, we must wait until he has had an opportunity of repeating his experiments under conditions that preclude any possibility of error either in his methods or in the interpretation of his results. If he succeeds in maintaining his present position, there will be offered to us a ready explanation of many geological phenomena, among them the crystallisation of minerals at considerable depths under the surface of the earth.

W. S. B.

Some Recent Text-books on Chemistry.

A text-book which passes through ten editions in sixteen years must have good qualities. This remark certainly is applicable to Attfield's Chemistry,[1] a book which is so well known that it is hardly necessary to do more than note the appearance of this new and improved edition. It seems, however, desirable to point out that feature of the book which, in all probability, has made it so popular. There can be little doubt that it is its thoroughly practical character, the expression being used in the best sense. The author understands what the student ought to learn, and is able to put himself in the student's place and to appreciate his state of mind. Instead, therefore, of serving up a lot of "fundamental principles" to begin with, he skillfully brings the student in contact with the most important substances, and shows him how to study the most important reactions for himself. Instead of restricting his laboratory work to such reactions as may happen to be important for analytical purposes—in other words, instead of emphasising precipitates and disregarding the things unseen, as is too commonly done, he gives excellent directions for the study of synthetical reactions. Thus, under the head of Potassium, the student is shown how in test-tubes to *make* caustic potash, potassium bicarbonate, potassium iodide, the manganates, etc. So also in connection with the other elements, the chief compounds are treated in a similar way. Many of the compounds are, to be sure, introduced prematurely, the reason for this being the fact that they

[1] Chemistry: General, Medical and Pharmaceutical, including the chemistry of the U. S. Pharmacopœia. A Manual of the general principles of the science, and their applications in Medicine and Pharmacy. By John Attfield, F. R. S. 10th Edition. 8vo, 728 pp. Philadelphia: Henry C. Lea's Son & Co., 1883.

are used in medicine. This interferes with rather than enhances the value of the book. Thus again, under Potassium, we have the acetate, citrate, tartrate and the acid tartrate treated. So too, under Lead, we find oleate of lead, etc. Such treatment can only tend to confuse the student.

The part of the book which treats of "Organic Chemistry" has an antique flavor. The writer cannot be familiar with the present state of the subject. We don't ask him to cover his pages with structural formulas, but we do ask him to give the student some slight advantage of the beautiful and simple system of classification which is the result of modern studies of the compounds of carbon. He has given us a remarkable jumble.

A second American edition of Würtz's Chemistry[1] has appeared, the first bearing the date 1879. The commanding position occupied by Professor Würtz among chemists is a guarantee that his book is a valuable one. We examine it mainly with the object of seeing how a master deals with the subject. We may feel sure that the method of presentation adopted is the result of deliberate thought, based upon most comprehensive knowledge and experience in teaching. And what is the result? Does the author begin with an elaborate explanation of bonds and valence and structure and radicals and substitution? By no means. These subjects are not touched until page 222 is reached, and then cautiously—not dogmatically. It must be remembered that the author is one of the most ardent champions of modern structural chemistry, that he has himself done a great deal towards the development of the views now so commonly held. Yet he clearly sees the relations of these views to the facts, and his method of teaching is well calculated to keep these relations clearly before the mind of the student. The general introduction of the book would be of benefit to science.

Here and there occurs a dogmatic statement without explanation, as for example on page 106: "It (hydroxyl) is a monatomic group, and sulphuric acid is formed by the saturation of the affinity of the diatomic radical sulphuryl by two monatomic groups hydroxyl, which replace the two atoms of chlorine of sulphuryl chloride." . . . "The sulphur in sulphuric acid is *hexatomic*." Further, on page 13, is found this paragraph: "The molecules of oxygen . . . are each formed of two atoms," etc. Of course, to one well advanced in the subject there is nothing startling in such statements, but, to the beginner with no preparation, how must they appear?

We venture to express the hope that in future editions the translator, whose work in the main is well done, will adopt the system

[1] Elements of Modern Chemistry. By Adolphe Würtz. Second American edition, translated and edited, with the approbation of the author, from the Fifth French edition, by Wm. H. Greene, Professor of Chemistry in the Philadelphia High School. London and Philadelphia: J. B. Lippincott & Co. 1884. 8vo, 770 pp.

of nomenclature proposed by Professor Watts for the use of those who prepare the abstracts for the Journal of the (English) Chemical Society. The suffix "ol" which the translator uses in the names benzol, toluol, xylol, &c., might better be reserved for bodies of alcoholic character. The English names most commonly used are benzene, toluene, xylene, &c.

Professor Richter's book has acquired a deserved popularity in Germany, and we are glad to welcome the American edition[1] which has been prepared by Professor Smith. The two features of the book which call for special mention are the use of the periodic law, especially as developed by Mendelejeff, as the basis of classification, and the treatment of the thermo-chemical phenomena involved in the principal reactions. There is much to be said in favor of the method of classification adopted. It cannot be applied rigidly and the author has not attempted to. He begins with hydrogen, and then takes up successively the halogen group, the oxygen group, the nitrogen group and the carbon group. In the nitrogen group are included phosphorus, arsenic, antimony, vanadium, niobium and tantalum. Bismuth is not included because its "metallic character . . . considerably exceeds its metalloidal."

At the end of the chapter on each group there is given a brief statement in regard to the thermal relations. It is time that the student's attention should be directed towards the thermal phenomena, so that, though the subject may not be fully developed, he may at least know the general character of the results already obtained and their bearing upon the science. It certainly is true that we do not as yet know enough about these complicated phenomena to warrant our using them as the basis of a strict scientific treatment of chemistry, but that should not prevent our teaching some of the simpler facts of the subject. The author first refers to the fundamental law according to which, when substances are brought together, that reaction takes place which gives rise to the greatest evolution of heat (the principle of greatest work). Of course, if this law were strictly true and without exceptions, and if we knew the heat evolved in the formation of every compound, it would be possible always to predict what the result of bringing together any given elements or compounds must be. Unfortunately, the law appears at times to fail, and, notwithstanding the labors of Thomsen, Berthelot and others, our knowledge concerning the figures representing the heat of formation of a very large number of compounds is exceedingly imperfect or entirely wanting, so that we cannot as yet make general use of the principle of greatest work, though probably the time is approaching when this will be possible. It is to be hoped that teachers of chemistry

[1] A TEXT-BOOK OF INORGANIC CHEMISTRY. By Prof. Victor von Richter. Authorised translation of Third German edition, by Edgar F. Smith, Professor of Chemistry in Wittenberg College, Ohio. Philadelphia: P. Blakiston, Son & Co. 1883. 8vo, 424 pp.

may prepare their students for the change by impressing upon their minds the importance of thermo-chemical phenomena.

A more careful use of English would have improved the translator's work and made the book more valuable for students. Many of the sentences are obscure in consequence of literal translation. In some cases words are incorrectly rendered. On pages 142, 144, for example, the two first members of the marsh gas series of hydrocarbons are called *methyl* and *ethyl*, instead of *methane* and *ethane*. The names used apply to the radicals CH_3 and C_2H_5 respectively, as is well known.

Finally, we cannot pass over a book[1] by Edwin J. Houston, inasmuch as it illustrates a tendency which is highly objectionable in the teaching of chemistry. The author begins with a consideration of theories which cannot be comprehended until chemical facts have been studied. He has evidently endeavored to make a book which can be used in "recitations." The sentences are short and are intended to be learned by heart. They are for the most part correct enough, but, as a rule, they are not adapted to the use of the beginner. When a boy is about to begin the study of chemistry, it not only does no good, but it does positive harm, to make him learn a lot of definitions of words. Give him the things so far as possible; don't muddle his mind with words more than is absolutely necessary. One cannot avoid a feeling of indignation on reading in the introductory part of a book on elementary chemistry, such bald definitions as:

"*Acids are substitution compounds formed by the combination of an electro-negative substance with hydroxyl.*"

"*Bases are substitution compounds formed by the combination of an electro-positive substance with hydroxyl.*"

"*Salts are substitution compounds in which an electro-positive radical or element is united to an electro-negative radical or element by means of oxygen.*"

These definitions are merely so many high-sounding words. They do not convey any sort of an idea to the mind concerning the nature of the substances defined. This kind of teaching is, we are happy to say, fast losing ground, but the appearance of this book arouses a fear that it still may be in more extensive use than we hoped.

It is unnecessary to go into details regarding the faults of the book. If any one should decide to use it, we earnestly advise the omission of all that pertains to chemical theories. The treatment of the facts is fairly good, but we cannot see that it is any better than that of a dozen other elementary text-books now in use.

I. R.

[1] THE ELEMENTS OF CHEMISTRY. For the use of Schools, Academies and Colleges. By Edwin J. Houston, Professor of Physical Geography and Natural Philosophy in the Central High School; Author of "Elements of Physical Geography," "Elements of Natural Philosophy," etc., etc. Philadelphia: Eldredge & Brother. 1883. 8vo, 444 pp.

REPORT ON GLUCOSE, prepared by the National Academy of Sciences, in response to a request made by the Commissioner of Internal Revenue. Washington, Government Printing Office, 1884.

This report contains a great deal of information in regard to the manufacture of starch-sugar and the nature of the products obtained. There are twenty-nine factories in the United States, using, as nearly as can be estimated, 43,000 bushels of corn per day. The products are of various grades, which appear in commerce under the following names: (*a*) The liquid varieties: Glucose, mixing-glucose, mixing-sirup, corn-sirup, jelly-glucose, confectioners' crystal glucose. (*b*) The solid varieties: Solid grape-sugar, clipped grape-sugar, granulated grape-sugar, powdered grape-sugar, confectioners' grape-sugar, brewers' grape-sugar.

The most general purposes for which starch-sugar is used are: 1. For the manufacture of table-sirup; 2. A substitute for barley-malt in the brewing of ale or beer; 3. As a substitute for cane-sugar in confectionery; 4. For the adulteration of cane-sugar, to which it is added to the extent of 20, or more, per cent.; 5. For the manufacture of artificial honey; 6. For the manufacture of vinegar.

The transformation of the starch into dextrose is effected in most of the factories by means of sulphuric acid, though in some oxalic is used, and the use of phosphoric acid has been suggested. The normal products of the transformation by means of these acids are, as is well known, dextrose, maltose and dextrin. The commercial products consist of these substances in different proportions, the liquid products containing more dextrin and maltose than the solid products. In the latter the analyses showed the presence of from 72 to 73.4 per cent. of dextrose, and from 4.2 to 9.1 per cent. of dextrin. In the "glucoses" or liquid products analysed, the amount of dextrose was found to vary from 34.3 to 42.8 per cent., and the amount of dextrin from 29.8 to 45.3 per cent. The mineral constituents were found to be present only in insignificant quantities and to be of harmless nature.

In the fourth subdivision of the report the subject of the relation of starch-sugar to health is discussed. The question, "Is the use of 'glucose,' or 'grape-sugar,' injurious to health?" is asked, and the report then proceeds:

"This is certainly one of the most important questions that can be asked regarding the substance under consideration. It has been discussed very freely, but on a very insufficient basis of facts. Indeed, so far as the products made from corn-starch are concerned, it appears that no experiments have ever been made with reference to their effects upon the system. It is essential in a discussion of this subject to keep clearly in mind the fact, that while it is undoubtedly true that the pure chemical substances, dextrose, maltose, and dextrin, are not injurious, there may be other substances present in

small quantities in the commercial products, and that these are capable of producing injurious effects; or it may be true that when the commercial products are changed by fermentation, substances of injurious character are formed or left unfermented.

"In Germany, where large quantities of dextrose are made from potato-starch, experiments bearing upon the question of the presence of injurious constituents have been made with the commercial products. Some of the results obtained indicate that after fermentation of potato-sugar there are left substances which are injurious, while others indicate that this is not true. Among those who have experimented on the subject, A. Schmitz, Nessler, and Freiherr von Mering should be specially mentioned. Schmitz[1] fermented potato-sugar, and, evaporating the products down to small volumes, administered known quantities of the residues to cats and dogs, and in a few cases to human beings. The results obtained were uniform, and showed that the substance caused sickness, as headache, sweating, and loss of appetite.

"Later, Nessler[2] undertook similar experiments, and obtained similar results. He experimented upon his assistant and himself. One of his experiments is here described. He allowed a 20 per cent. solution of potato-sugar to ferment after the addition of a small quantity of hops. After the fermentation was over, the liquid was filtered, a litre evaporated down to a sirup, and then diluted up to 100 cc. This solution had a disagreeable, bitter taste. Nessler took 50 cc. of it at 7 A. M., and the same quantity at 10 A. M., each portion corresponding to 100 grams of potato-sugar. Toward noon he began to feel uncomfortable, but not so much so that he could positively attribute his condition to the beer extract. At 2 P. M., the residue from 100 grams potato-sugar was again taken; and now in about an hour there followed profuse perspiration and violent headache, both of which continued until night. A few days later, his assistant took the residue from 90 grams of sugar, the fermented liquor having been evaporated down to two-fifths its original volume. He soon experienced difficulty in breathing and broke out in a cold sweat; at dinner he had no appetite, and was obliged to throw up the little soup he did take. In the afternoon he had a violent headache, which continued until evening.

"Nessler concludes his paper with these words: 'It is hence beyond a doubt true that in the liquid obtained in the fermentation of potato-sugar there are substances injurious to health. If the question is asked whether this is true of all commercial potato-sugars, as well as of the sugar examined, we cannot give a definite answer.

"'In the case of all varieties of potato-sugar thus far examined, there remains after evaporation of the fermented liquid a bitter-tasting extract, which turns the plane of polarisation to the right,

[1] Beiträge zur diätetischen Beurtheilung des gallisirten Weines. Bonn, 1878.
[2] Wochenblatt des landwirthschaftlichen Vereins im Grossherzogthum Baden, 1880.

and it is very probable that all of them may act injuriously upon the health, in varying degrees, according to the greater or less purity.

"'As in buying the sugars it is not possible to determine whether the harmful substances are present or not, potato-sugar should not be used for the preparation of beverages,[1] until it can be prepared in perfectly pure form.'

"Directly opposed to the results of Schmitz and Nessler are those obtained by Freiherr von Mering.[2]

"This writer experimented upon dogs, cats, rabbits, and human beings, in much the same way as Schmitz and Nessler had done, and he concludes that the unfermentable residues from potato-sugar are not at all objectionable.

"Later, Schmitz[3] replied to Von Mering, upholding his first results.

"It hence appears doubtful whether there are injurious substances in potato-sugar, and it is highly desirable that the experiments on this subject should be repeated by those who have not thus far taken active part in the discussion. Even though it should eventually be shown that potato-sugar is or is not objectionable, it would not necessarily follow that the same is also true of maize-sugar.

"As, so far as we know, no experiments had been made upon starch-sugar, we carefully repeated the experiments described above, using several of the samples of glucose and grape-sugar, the analyses of which are given in the preceding part of this report.

"We were fortunate in securing for this work the assistance of Dr. J. R. Duggan, of the Johns Hopkins University, who has for some time past been occupied in experiments upon fermentation, and who is hence fully familiar with all the precautions necessary to secure reliable results. The fermentations were carried on in a new cellar, which fortunately chanced to be available, so that the danger of abnormal fermentation was reduced to a minimum.

"Pure glucose cannot be fermented by the simple addition of yeast in small quantity; for yeast, like all living matter, requires certain nitrogenous and inorganic materials for its own nourishment. As has been shown by Pasteur, this want may be supplied by the addition of certain salts, such as ammonium tartrate, calcium phosphate, &c.; but as these cannot be added in exactly the necessary proportions, some would be likely to remain in the solution after fermentation was complete, and, if taken into the stomach along with the glucose residue, would probably produce an effect of its own which might be attributed to the glucose.

"It is not easy to obtain in sufficient quantity a liquid furnishing a proper medium for the growth of yeast which does not also contain glucose; and, for this reason, it was first necessary to deter-

[1] One of the uses to which potato-sugar is put in Germany is as an addition to poor wine.
[2] Deutsche Vierteljahrschrift für öffentliche Gesundheitspflege, **14**, 325. [3] *Ibid.* 481.

mine the effect, if any, of the unfermentable residue from this glucose.

"Experiments Nos. 1, 2, and 3 were made for this purpose. The nutrient liquid used was barley-wort, on account of the fact that it is most commonly used in brewing for commercial purposes.

"This liquid contains much more nitrogenous matter than is necessary to support the yeast during its fermentation, and therefore it still forms a good medium for the growth and development of yeast after it is considerably diluted with a solution of glucose.

"The method of experimenting was as follows: The barley-wort, of the concentration usually employed for making beer, was mixed with the glucose solution, and the whole heated to boiling by passing steam through a coil of block-tin tubing placed in the tub. The tube was then connected with the hydrant, and water passed through it until the solution was well cooled. It was then allowed to flow slowly over a wide board, for the purpose of thoroughly aerating it. The temperature was reduced to about 10° C., and about a pint of yeast added. Fermentation was carried on in a cool vault, and was allowed to continue until very little sugar was left in the solution and the yeast had all settled to the bottom of the tubs. A sufficient quantity of beer was then siphoned off and evaporated slowly over the water-bath to about one-tenth its volume. The residue consisted principally of dextrin, nitrogenous matter from the wort, glycerin, succinic acid, and probably other products of fermentation in very small quantities. It formed a thick, dark-colored sirup, of very disagreeable taste, especially when wort containing hops had been used. For this reason, sweet-wort was used in most of the experiments. All of the fermentations were carried on by the low process—that is, with bottom yeast at a temperature of from 8° to 10° C.

"Two experiments were tried with the high process, but it was found to be impracticable on the small scale, on acconnt of the development of bacteria, due to the higher temperature. As the difference in the two processes is essentially one of temperature only, there is no reason to suppose that they could in any way give different results.

"The amount of yeast added to each tub was about one-half litre. This was carefully examined with the microscope, both before and after fermentation, to guard against the presence of foreign ferments that might produce injurious products. The glucoses used were of the various manufactures already mentioned, and embraced the different grades of solid and liquid products.

"The extracts were taken at different hours of the day, both before and after meals. The quantity usually taken contained the residue from 125 grams of glucose; but in experiment No. 8 this quantity was increased so as to correspond to 200 grams. It seems useless to try still larger quantities, for it is probable that if much more was taken the normal products of fermentation, such as succinic acid, would produce some effect.

"*Experiments* 1 *and* 2.—Thirty litres of sweet-wort and the same quantity of hopped wort were separately fermented, the process lasting, in each case, one week. Five litres of the resulting liquid were evaporated to 750 cc., and 300 cc. of the extract taken internally. The same experiment was tried by two individuals, but no effect was produced. The amount of extract taken corresponded to two litres of the beer.

"*Experiment* 3.—In this experiment there were used 15 litres of sweet-wort, to which were added 15 litres of a 12.5 per cent. solution of cane-sugar. Five litres of the liquid were evaporated to 500 cc., and 200 cc. of the extract taken, with no effect. The amount of extract taken represented 125 grams of cane-sugar.

"*Experiment* 4.—Fermented 15 litres sweet-wort and 15 litres of a 12.5 per cent. solution of grape-sugar. (Sample No. 12.) Five litres of the liquid were evaporated to 500 cc., and 200 cc. taken. No effect was produced. On the following day, the same amount of residue was taken, and with no effect. The amount of extract taken corresponded to 125 grams of glucose in each experiment.

"*Experiment* 5.—Fifteen litres of sweet-wort and 15 litres of a 12.5 per cent. solution of grape-sugar (Sample No. 7) were fermented. The same amount of extract was taken as in the last experiment, with the same results.

"*Experiment* 6.—The details of this experiment were exactly the same as those of the last. The substance was a commercial glucose. (Sample No. 14.)

"*Experiment* 7.—Fifteen litres of hopped wort, with 7.5 litres of a 25 per cent. solution of commercial glucose (Sample No. 1), were fermented. Four litres of the fermented liquid were evaporated down to 400 cc., and of the residue 150 cc. were taken. No effect was felt.

"*Experiment* 8.—Fifteen litres of hopped wort and 7.5 litres of a 25 per cent. solution of grape-sugar (Sample No. 13) were fermented. Five litres of the fermented liquid were evaporated to 500 cc., and 200 cc. taken. No effect was felt. The extract represented 160 grams of grape-sugar.

"The experiments described above occupied about two months, during which time Doctor Duggan repeatedly took large quantities of the extracts. At the end of the experiments, and during the entire period, his health continued excellent.

"There was nothing whatever to indicate that the extracts contained anything injurious to health, and the conclusion seems to be fully justified that the samples examined by us, and which we have every reason to believe were fair average samples of the substances found in the market, contained nothing objectionable from a sanitary standpoint. In the experiments the experimenter took into his system everything that could possibly be objectionable contained in from 120 grams to 160 grams of the glucose, or

grape-sugar, *i. e.*, from a quarter to a third of a pound. It must be borne in mind, further, that the extract which was taken into the stomach must have contained any objectionable mineral as well as organic substances present in the glucose employed. Hence, the results seem to be final as regards the injurious nature of glucose, or grape-sugar, made from maize.

"These experiments extended over a period of only about two months. On the question, therefore, whether any injurious effect would follow the continuous use of this material, the committee has no information.

"Our experiments have, of course, no direct connection with those of Schmitz, Nessler, and Von Mering, already referred to. These gentlemen experimented upon potato-sugar as furnished by manufacturers in Germany. Our conclusions are valid only for maize-sugar as furnished by manufacturers in this country.

"It should be further remarked that, although our experiments show conclusively that the products of fermentation of glucose are not dangerous to health, it does not necessarily follow that beer made by the fermentation of glucose is as good as that made in the usual way. That is a matter which does not fall within the scope of our investigation."

The report was prepared by a committee of the National Academy of Sciences, which consisted of Professors George F. Barker, of the University of Pennsylvania; W. H. Brewer, of Yale College; Wolcott Gibbs, of Harvard College; Charles F. Chandler, of Columbia College; and Ira Remsen, of Johns Hopkins University.

ON THE DISCOVERY OF THE PERIODIC LAW, AND ON RELATIONS AMONG THE ATOMIC WEIGHTS. By JOHN A. R. NEWLANDS, F. I. C., F. C. S., etc. London: E. & F. N. Spon. 8vo, 39 pp.

This book has been published in order to place before chemists the proof that the author was the first one to point out the existence of the periodic law relating to the properties of the elements as functions of their atomic weights. In the preface the author says: "This little book contains an exact reprint of all the papers on Relations among the Atomic Weights, and on the Periodic Law (provisionally termed the 'Law of Octaves'), written by myself, and printed in the *Chemical News*, some years before M. Mendelejeff had published anything on the subject of the Periodic Law. . . .

"Having been the first to publish the existence of the periodic law more than nineteen years ago, I feel, under existing circumstances, compelled to assert my priority in this matter.

"That both Mendelejeff and Lothar Meyer have done a good deal to develop the periodic law is admitted, but this admission by no means assumes that either of these eminent chemists was the

first discoverer of the law in question. As a matter of simple justice, and in the interest of all true workers in science, both theoretical and practical, it is right that the originator of any proposal or discovery should have the credit of his labor. . . .

"To sum up: I claim to have been the first to publish a list of the elements in the order of their atomic weights, and also the first to describe the periodic law, showing the existence of a simple relation between them when so arranged."

A careful examination of the republished papers shows that the author really had a fairly clear notion of the periodic law as far back as 1864, while, as is well known, the papers of Mendelejeff and Lothar Meyer appeared in 1870.

The state of the case appears to be about as follows: Several chemists prior to 1864 had pointed out simple relations between the atomic weights of certain groups of similar elements, as sulphur, selenium and tellurium; chlorine, bromine and iodine, etc., etc. Then Newlands arranged all the elements in one table, mainly with the object of showing numerical relations between the atomic weights. In a communication to the *Chemical News*, dated August 18, 1865, Mr. Newlands said: "If the elements are arranged in the order of their equivalents, with a few slight transpositions, as in the accompanying table, it will be observed that elements belonging to the same group usually appear on the same horizontal line." In the table referred to the symbols H, F, Cl, Co and Ni, Br, Pd, I, Pt and Ir, form the first horizontal line. While, thus, fluorine, chlorine, bromine and iodine appear in the same line, cobalt and nickel, palladium, platinum and iridium are also found in this line, a fact which would lead one to suspend judgment in regard to the value of the proposed table. Mr. Newlands in the same paper says: "It will also be seen that the numbers of analogous elements generally differ by 7, or by some multiple of 7; in other words, members of the same group stand to each other in the same relation as the extremities of one or more octaves in music." The numbers here mentioned are those designating the position of the elements in the table. Thus, hydrogen is 1, lithium 2, glucinum 3, boron 4, &c., and the above statement is the first one bearing upon the fundamental principle involved in Mendelejeff's and Lothar Meyer's tables, viz. that the elements naturally fall into groups of seven, each eighth having properties similar to those of the first in the series. For this discovery Mr. Newlands should certainly receive credit. It is, however, doubtful whether, without much greater development, the periodic law would have received the serious attention of chemists. While the arrangement in groups of seven is made use of by M. Mendelejeff, that really forms only the simplest part of his system. The fact first pointed out by Mendelejeff that two such short series of seven elements, together with a sub-series of three others, combine to form a long period, alone makes it possible to arrange all the elements in one table in such a way as to bring allied elements

together. When this fact was discovered what wonderful results followed! When the relations which exist between the atomic weights and the properties of the elements were so clearly pointed out by M. Mendelejeff, chemists no longer doubted. They saw at once that a law of fundamental importance had been discovered. As regards the question whether the law in its perfected form was first discovered by M. Mendelejeff or by Lothar Meyer, it seems to be true that these chemists were working on the subject in much the same way at the same time, but that, as a matter of fact, Mendelejeff's paper was published, or at least read publicly, a few months before Meyer's appeared. The names of both these gentlemen will certainly always be remembered in connection with the periodic law, and that of Mr. Newlands cannot well be forgotten.

I. R.

NOTES.

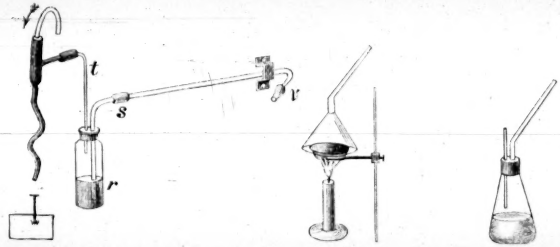
To remove Noxious Vapors in the Evaporation of Corrosive Liquids.

In the chemical laboratory of Vassar College, a Richards aspirator with the necessary water supply and waste pipes is furnished to every student. It is used not only for rapid filtration, but in other processes wherever a current of air is needed. I have also applied it to the process of evaporation, first, for the purpose of carrying away the noxious vapors arising from corrosive liquids, and second, for evaporation in partial vacuo.

To fit the aspirator for general use it is mounted upon one corner of the student's work-table in the manner shown in Fig. 1. A small glass tube *t*, joined to the exhaust pipe by rubber tubing, passes through the air-tight cork of an eight-ounce wide-mouth bottle. A larger tube reaches nearly to the bottom of this bottle. The tube *sv* is a little smaller and enters the end of this larger tube, while a piece of rubber tubing stretched over the junction makes a tight but flexible joint. The outer end at *v* has a rubber tube stretched over it, by means of which connection is made with whatever apparatus is to be exhausted. Disconnection is made at this point *while the aspirator is still running*, to prevent the water from the bottle *r* backing over into the vacuum which has been produced in the filter bottle or other vessel employed.

The Ventilating Funnel.—The stem, six or eight inches long, of a glass funnel is bent at a right angle near the body. The end of the stem is thrust through the rubber tubing, and into the some-

what larger tube *v*. The evaporating dish is then brought up under the mouth of the funnel until the funnel rests upon it (Fig. 2). The aspirator is then started and the heat applied. The current of air flowing over the edge of the evaporating dish into the funnel



carries the fumes with it to be condensed in the reservoir bottle *r*, or off with the stream of water into the sink. The edge of the funnel may rest *inside* the evaporating dish with the same result; the same funnel is thus used with dishes of varying diameter. Two sizes are at present in use; one of 3 inches diameter for evaporating dishes, another of 1½ inches for crucibles. The evaporation of acids to dryness is conducted on the open tables without annoyance from their fumes, by means of this simple artifice.

The Flask.—Let the cork of a flask be pierced with two holes, one for a bent tube to enter the aspirator tube *v*, the other for a straight tube which may be adjusted so that its lower end will be little above the liquid within. A current of air will then pass through this straight tube, over the surface of the corrosive liquid in the flask and sweep its fumes away into the waste.

To evaporate in partial vacuo, provide the flask with a cork carrying the bent tube only. No air can enter, and the aspirator will then create a vacuum, to a degree depending on the head of water at command.

LE R. C. COOLEY.

VASSAR BROTHERS LABORATORY OF VASSAR COLLEGE, *March*, 1884.

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F. W. C.